Recirculation of the Mo-99 research loop

Predicting the long-term behaviour of the the loop content

by

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Abstract

The widely used medical isotope, molybdenum-99, is produced in only 5 nuclear reactors worldwide. Those reactors are all at least 40 years old. If one of them shuts down this will cause major problems in the supply chain of ^{99}Mo. To secure the supply of this isotope, several studies are done for designing new methods to produce ^{99}Mo. One of them is the ^{99}Mo research loop in the Hoger Onderwijs Reactor (HOR), Delft. By combining the production and processing steps of the supply chain, this method will provide a more efficient way of producing ^{99}Mo.

A U-shaped tube, filled with uranyl nitrate, will be inserted in an existing tube near the reactor core. When this salt runs through the tube it is irradiated by the neutrons from the core. By the decay of several fission products, ^{99}Mo is produced. The isotope will be separated immediately as it leaves the reactor, allowing for the ^{99}Mo bulk liquid to be transported to hospitals very quickly. Since the isotope has a half-life of only 66 hours, this can minimize the product loss significantly. If the implementation in the HOR is successful, this method could also be implemented in other reactors.

This study focusses on the long-term behaviour of the loop content when the salt is recirculated for several years. During this period the uranium is consumed and different fission products start to build up. In order to simulate these effects, a Serpent code is used. This code is capable of calculating the composition of the loop content after an irradiation time of several days. With these results an analytical model is made to predict the behaviour after many years.

The created model has a deviation of 5% with respect to the simulation results from Serpent. This accuracy is considered sufficient to make a good estimation of the durability of the loop content. From the predictions it can be concluded that after 22 years, the production of ^{99}Mo will still be 80% of the initial production.

In addition, the influences of the strong reactor poison ^{135}Xe are studied. When this isotope and its main parent, ^{135}I, are filtered from the system, this could lead to higher production values of ^{99}Mo. It is found, however, that the effects of filtering on the production of ^{99}Mo are not significant.

Contents

1 Introduction

1.1. Molybdenum-99

Molybdenum-99 is the decay parent of a widely used medical isotope, Technetium-99m. This isotope is applied in over 80% of the radio pharmaceuticals [5] as a tracer in the body and is ideal for creating high quality images using low radiation doses. ^{99}Mo is formed by the decay of several fission products from uranium-235.

To produce ^{99}Mo, uranium targets are irradiated in a nuclear reactor (steps 1 and 2 in figure 1.1). The irradiated targets are then processed in a ^{99}Mo facility and the resulting purified ^{99}Mo will be distributed to ^{99}Mo-^{99m}Tc generator facilities (steps 3 and 4) where the bulk liquid is loaded onto small generators. Because ^{99m}Tc only has a half-life of six hours, these generators need to be stored inside the hospital where the technetium can be extracted and used immediately [9].

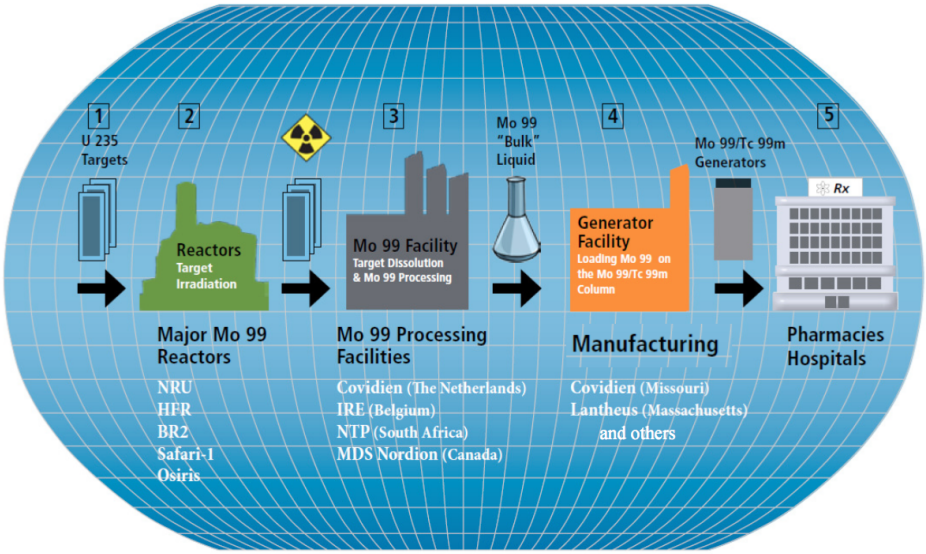

Figure 1.1: ^{99}Mo and ^{99}Tc supply chain. [5]

Despite the importance and common use of this isotope, ^{99}Mo is only produced in 5 nuclear reactors worldwide. Those reactors, in Belgium, the Netherlands, France, Canada and South Africa, are each at least 40 years old, but the complete supply chain depends on them. After one of the reactors shut down in 2010 for about half a year, the vulnerability of this supply was highlighted. This is why several researches were set up to find alternative ways for producing ^{99}Mo, one of them is the ^{99}Mo research loop in Delft.

1.2. Production of ^{99}Mo in the HOR

The Hoger Onderwijs Reactor (HOR) is a small pool-type research reactor (2 MW) operated by the Reactor Institute Delft (RID). The reactor is not built to produce electrical power, but is a source of neutrons and

positrons for research purposes [1]. K. Elgin studied the possibility of producing ^{99}Mo inside the HOR by irradiating uranium salt.

In his design [2], a U-shaped tube (figure 1.2) is placed inside an already existing tube, referred to as the DLDR beam-tube, near the core of the reactor. A solution of uranium salt is sent through this loop to be irradiated by the neutrons coming from the core. Inside this loop ^{99}Mo will be produced by the decay of several fission products of ^{235}U.

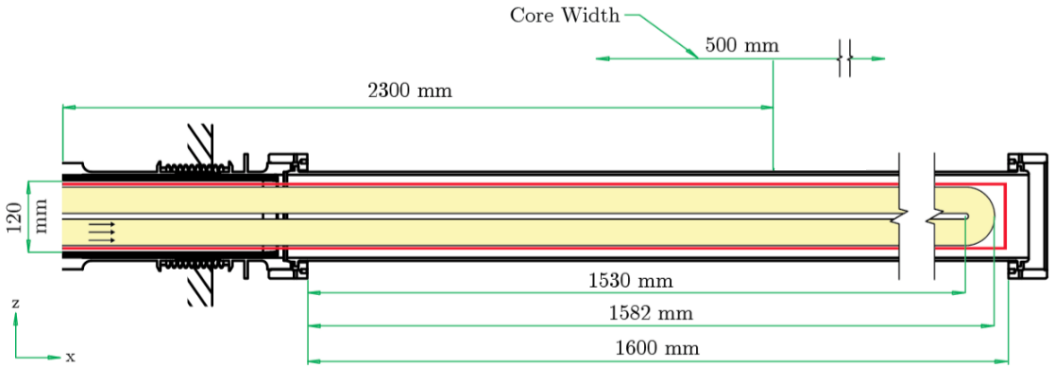

Figure 1.2: Cross section of the U-shaped tube. The uranium salt solution runs through the tube (yellow) and is irradiated by the neutrons coming from the core of the reactor to produce ^{99}Mo. [4]

The ^{99}Mo will immediately be separated from the salt as it leaves the reactor which means the production en processing steps mentioned in 1.1 are merged. This allows for a faster delivery of the ^{99}Mo, which is desirable since ^{99}Mo has a half-life of only 66 hours. When a faster delivery can be realised, less product will be lost before the generators reach the hospital.

If the implementation of this loop in the HOR is successful, a ^{99}Mo production of roughly 2%[1] of the worldwide demand could be achieved and the design can be implemented in other reactors to make a significant contribution to the supply of ^{99}Mo.

This report continues with the work done by Kenneth Elgin [2], Jurriaan Huisman [4] and Chris van Egmond [12]. Their progress will now shortly be summarised.

1.2.1. salt concentration in the loop

The solution that will be used in the tube is uranyl nitrate, as decided by Elgin [2]. Elgin showed with a simulation that high uranyl concentrations have a positive impact on the isotope production. It was concluded that the concentration should be as high as possible.

For the extraction of ^{99}Mo from the bulk liquid, separation columns are used. Originally alumina is applied as a sorbent for the solid uranium targets. However it was found that, when using uranium salt, the alternative sorbents Thermoxid and PZC lead to higher extraction performances. Thermoxid and PZC can still effectively extract ^{99}Mo from the salt when concentrations up to 310 g/L are used. This is why he decided 310g/L is the optimal concentration.

J.A.R. Huisman [4], who investigated the heat transfer in the loop, however discovered that when the concentration of uranyl nitrate is higher than 30g/L the content of the loop will start to boil. This heat is produced by fission reactions in the salt and gamma heating in the aluminium tube. In subsequent studies, including this report, a uranyl concentration of only 30g/L is used, in order to reduce the heat production from fission reactions. To create a more sufficient isotope production, the original concentration of 310 g/L is desired. Further research needs to be done on the heat production and heat transfer in the loop to be able to realise this.

1.2.2. Geometry of the tube

Before Huisman started his research a safety tube (indicated in red in figure 1.3) was added to the original design . This tube will function as a flood barrier in case a leak occurs in one of the other tubes.

[1] Based on a uranyl concentration of 310g/L in the loop. Further research needs to be done on heat transfer and heat production in order to realise this.

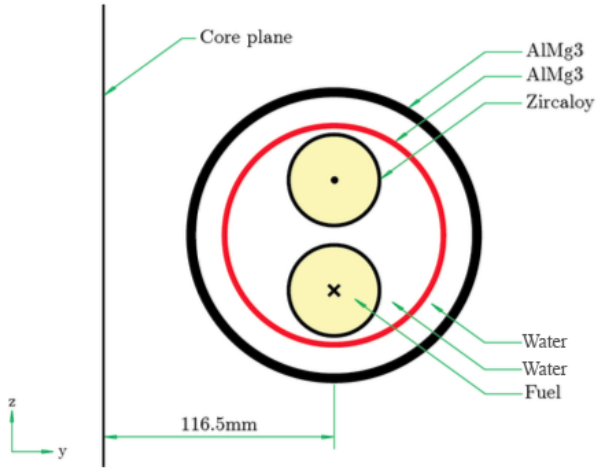

Figure 1.3: Cross section of the setup. The added safety tube, functioning as flood barrier, is indicated in red and both the DLDR and safety tube are filled with water to improve the heat transfer. [4]

In his study, Huisman also stated that heavy water should be added inside the DLDR and safety tube to improve the heat transfer of the system. This does absorb some of the neutrons, reducing the flux through the salt, but the improvement of heat transfer will allow for higher concentrations of uranyl in the loop. This will compensate for the lost neutron flux.

1.2.3. Simulations of ^{99}Mo and heat production in the tube

The software that was used for calculations of the ^{99}Mo production in the loop is Serpent. Serpent is a Monte Carlo based program used for burnup calculations in nuclear reactors.

For calculations concerning the heat transfer of the system, Huisman used COMSOL. This is a multi-physics program using Finite element Methods for solving various physics related calculations.

Van Egmond [12] studied the influence of the temperature on the isotope production. To combine the Serpent and COMSOL codes, he optimized the Serpent code and updated it to the latest tube design, including the safety tube and water. This Serpent code will be used as foundation for the simulations in this report.

For the complete simulation, Serpent is combined with matlab since Serpent can only calculate stationary situations. In Serpent, the geometry tube is divided into 12 sections and every step the complete content is irradiated for 15 minutes. Subsequently, matlab moves the liquid to the next section and adds new salt to section 1 (figure 1.4).

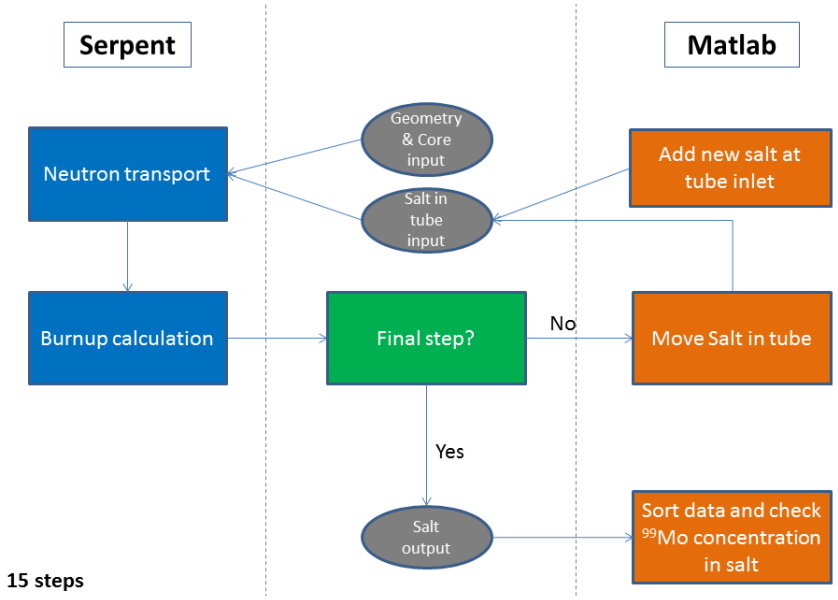

Figure 1.4: A schematic representation of the simulation. The loop is divided into 12 sections. Every step the salt is irradiated for 15 minutes before matlab moves the salt to the next section. This is repeated 15 times. The final output is processed with matlab to obtain useful data. [2]

2

Goals and outline

In prior researches the loop was studied for an irradiation time of 3 hours only, which is the time of a single circulation of the salt through the loop. With every step new salt was added to section 1. Since only a very small fraction of the uranium is consumed after one circulation, the salt can be recycled for a certain period before it is depleted. When irradiating the salt for a long time, different influences like the consumption of uranium and formation of fission products will start playing a role. Over time, the salt gradually wears out and will finally need replacement.

In this report, the long-term behaviour of the ^{99}Mo research loop is studied

2.1. Main goal

Before the loop design can be implemented in the HOR, an indication of the durability of the salt is desired. The main goal of this report is to predict the time that the content of the research loop can be recirculated before it wears out and needs replacement.

2.2. Secondary goals

Besides the main goal of this report, the influence of fission products on the ^{99}mo production is studied. ^{135}Xe is an isotope with a relatively high probability of absorbing neutrons. Since these neutrons could otherwise have caused the fission of uranium, the presence of ^{135}Xe is generally a bad influence on the performance of a system. The secondary goal of this report is to determine the effect of filtering all ^{135}Xe from the salt, in order to improve the ^{99}Mo production.

2.3. Outline

In order to continuously recirculate the content of the loop, the last section will be connected to the first. At the same time, a small flow is drained from the loop, filtered, and fed back. This way a constant supply of ^{99}Mo can be extracted.

To study the long-term behaviour of the loop, the original Serpent code is modified. A simulation that is capable of calculating several days of irradiation, while the content is recirculated, is obtained.

With the adjusted code, a coefficient can be determined that describes the consumption of uranium in the system. This can be used to create an analytical model for all materials of interest. With this model it is possible to predict the behaviour of the loop content on a time-scale of several years, without the limitations of computation time.

After the analytical model is validated by comparing it to the results from Serpent, an expression for the decrease of isotope production after several years can be obtained. Using this expression, conclusions are drawn about the durability of the salt and the influence of ^{135}Xe.

Finally the accuracy of the analytical model is discussed and some examples are given of further researches that can be done on this subject.

3

Theoretical background

3.1. Nuclear reactor physics

3.1.1. Nuclear chain reactions

For a good understanding of this report it is important to be familiar with some of the reactions occurring within a nuclear reactor. The principle of a nuclear reactor is based on a chain reaction starting with the collision of a neutron with the nucleus of a heavy element such as ^{235}U. This neutron can either be scattered or absorbed. When it is absorbed, this can lead to fission of the heavy nucleus, releasing new neutrons. These neutrons can in their turn cause new fissions [11].

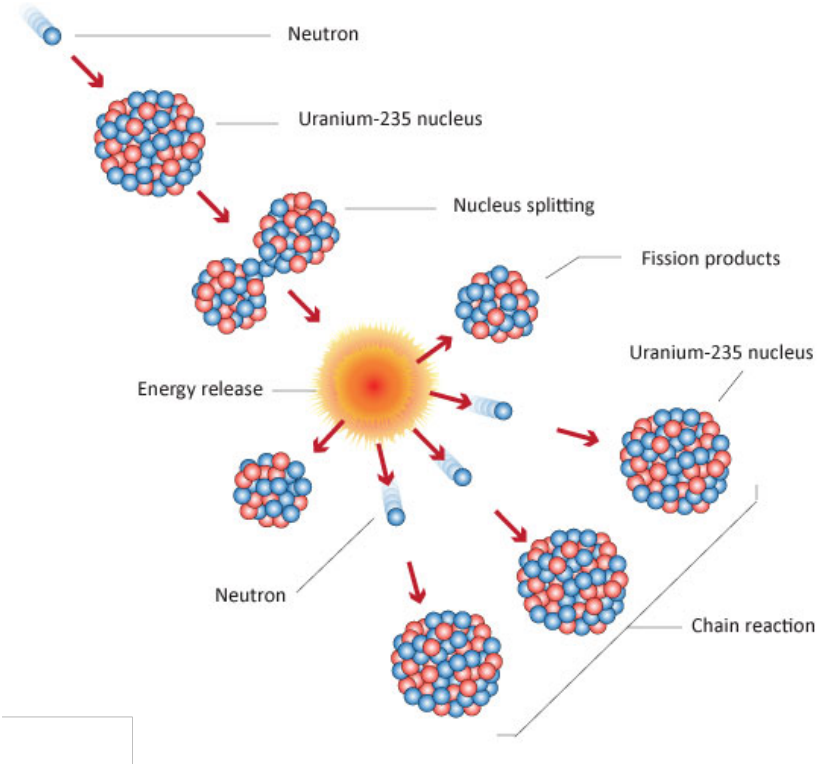

Figure 3.1: Illustration of a nuclear chain reaction [10].

3.1.2. Cross-sections

When a neutron collides with a nucleus, this event can result in the following three possible outcomes:

Scattering When scattering occurs, the neutron will simply scatter off the nucleus, either elastically or inelastically. When the scattering is elastic, no kinetic energy will be lost. With an inelastic reaction the neutron will shortly be absorbed by the nucleus and then be re-emitted. A gamma photon will be emitted in the process which means some of the kinetic energy is lost.

Capture In the event of collision, the neutron can be absorbed by the nucleus. In this occasion the neutron is either captured, or the nucleus is split in two smaller nuclei. When the nucleus and neutron merge and form one heavier nucleus, this is called capture. In this reaction a gamma photon will often be emitted as well:

$$^1n + ^A X \rightarrow ^{A+1} X + \gamma \tag{3.1}$$

Fission The third and most important outcome is fission. This reaction starts with the absorbsion of a neutron, turning the heavy nucleus briefly into an excited state. This state cannot be sustained and subsequently the nucleus splits into two smaller nuclei, releasing energy, gamma radiation and new neutrons. A fission reaction releases in general circa 200MeV, including the gamma radiation. In the following equation the heavy atom 'X' splits into two unknown fission products, Y_1 and Y_2. The identity of these fission products can be determined using the fission yield, which will be explained in section 3.1.3.

$$^1n + ^{A1}_{Z1} X \rightarrow ^{A2}_{Z2} Y_1 + ^{A3}_{Z3} Y_2 + \text{neutrons} + 200\text{MeV} \tag{3.2}$$

The probability for each of the three neutron-nucleus interactions to appear can be expressed with the cross-section σ. This quantity is measured in barn (1 barn = 10^{-14} cm^2) and can be considered as the effective target area a nucleus presents to a neutron [11]. Suppose a beam of neutrons with intensity I is projected onto a thin film of atoms with N atoms/cm^2, than the number of interactions C per cm^2 per second will be given by:

$$C = \sigma N I \tag{3.3}$$

This total cross-section can be divided into partial cross-sections for every separate neutron-nucleus reaction as indicated in figure 3.2. The total cross-section σ_t can simply be determined by adding all partial cross-sections together.

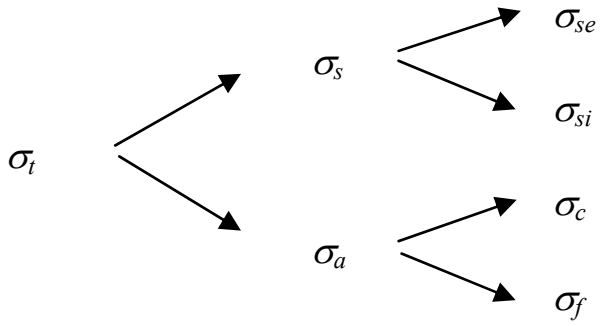

Figure 3.2: Microscopic cross-sections. $\sigma_t, \sigma_{se}, \sigma_{si}, \sigma_a, \sigma_c, \sigma_f$ are respectively the total cross section and the cross-section for elastic scattering, inelastic scattering, absorption, capture and fission. [11]

The neutron cross-section is affected by the energy of the neutrons. Fast, high energy neutrons have a lower likelihood of interacting with a nucleus than neutrons with low energy, called thermal neutrons. To slow down fast neutrons in reactors, heavy water is used as a moderator. In figure 3.3, the energy dependence of the fission cross-section is illustrated.

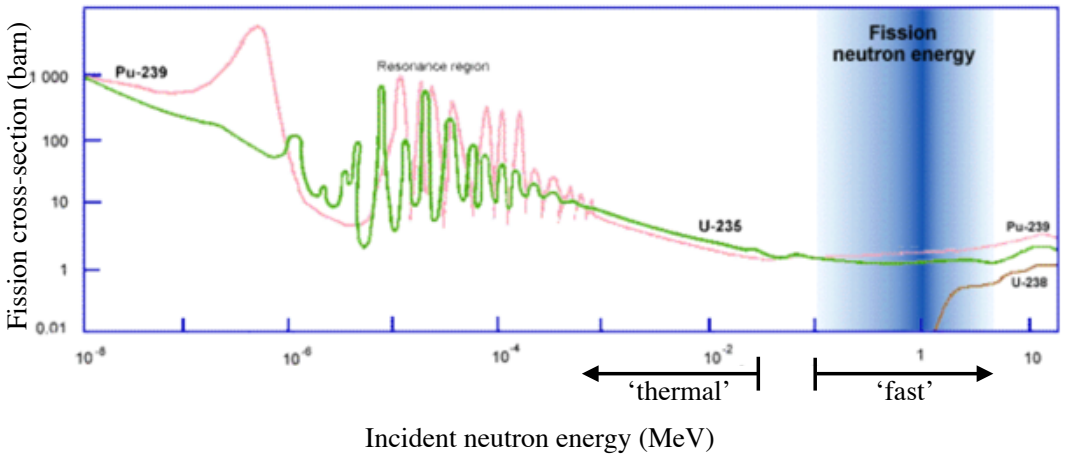

Figure 3.3: Energy dependence of the fission cross-section. It can be seen that fast neutrons have a low cross-section. In nuclear reactors, heavy water is used as a moderator to slow them down.

3.1.3. Fission yield

The Fission yield represents the probability a certain fission product will be produced. When the yield is plotted versus the mass numbers of possible fission products, it is distributed according to the camel curve (figure 3.4). Since the sum of the two new nuclei always equals the mass of the original nucleus, it can be seen by the trough halfway the x-axis that asymmetric reactions, where two fission products of different masses occur, are more probable than symmetric reactions, where two fission products with equal masses would appear.

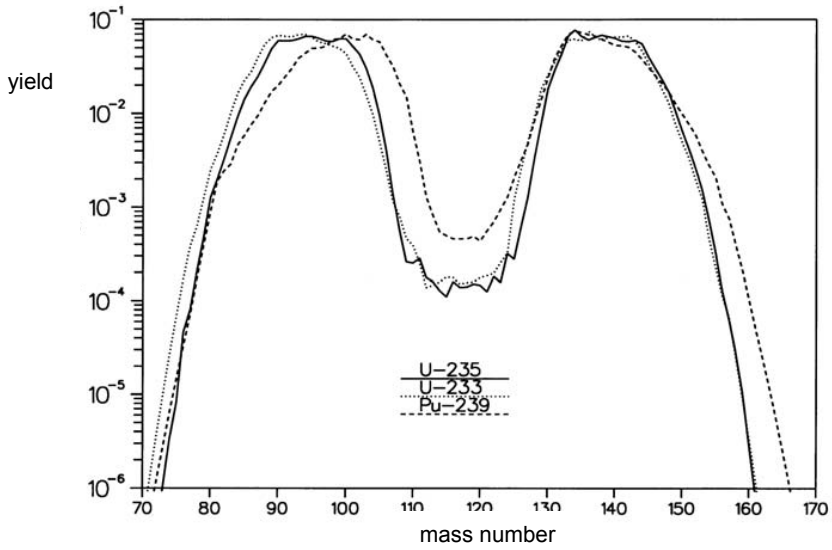

Figure 3.4: Camel curve: the yield of different fission products. The two peaks around the middle of the x-axis indicate that asymmetrical fission is most common. [11]

3.1.4. Radioactive decay

After a neutron-nucleus reaction, the remaining nucleus is generally still unstable. The fission products will decay into more stable states through α, β or γ decay, which is a form of radioactive decay. Usually multiple stages of β decay are needed to obtain a final, stable state.

3.1.5. Fuel composition

When a nuclear fuel is being irradiated with neutrons, its composition will gradually change over time. This is the result of fuel consumption, formation of new fuel and formation of fission products.

Consumption of nuclear fuel One of the long-term effects on nuclear fuel is consumption, also called burn-up, of the fissile nuclei. The ^{235}U concentration decreases due to neutron absorption. The absorption of neutrons can lead to either fission or capture, in both scenarios consuming the ^{235}U. This is why the absorption cross section (σ_a) and neutron flux (ϕ) determine the expression for the ^{235}U concentration ($U(t)$):

$$\frac{\mathrm{d}U(t)}{\mathrm{d}t} = -\sigma_{aU} U(t)\phi \tag{3.4}$$

Formation of new nuclear fuel Another long-term effect is the formation of new nuclear fuel by conversion of fertile material. This is a process where non-fissile products convert to fissile products by $\beta-$decay. An important example of this phenomenon is the formation of Plutonium-239:

$$^{238}U +^{1} n \rightarrow^{239} U \rightarrow^{239} Np \rightarrow^{239} Pu \tag{3.5}$$

Formation of fission products On a shorter time scale, many fission products are formed through fission and decay. Because it is impossible to consider al of them analytically, the computer program Serpent can be used for accurate calculations. However, the production of the most important fission product, Xenon-135, will be explained.

All fission products have a certain absorption cross-section indicating how many neutrons they absorb. Fission products with a high absorption cross-section diminish the burnup process by absorbing neutrons that would otherwise react with the uranium. The 'reactor poison' Xenon-135 is an important example with a very high cross-section and is mainly produced by the decay of Iodine-135. The production of ^{135}Xe can be illustrated in a scheme (figure 3.5) that indicates several fission and decay events.

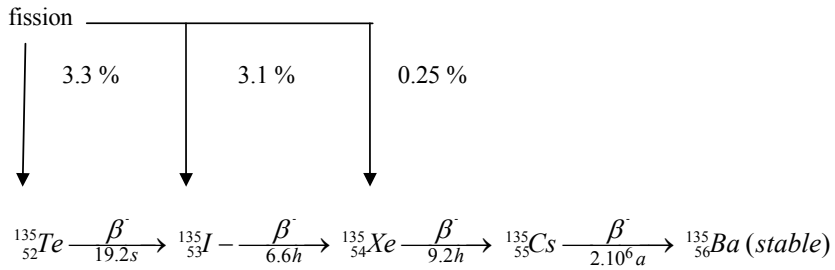

Figure 3.5: Process of fission and decay leading to Xenon-135 with indicated fission yield and half-life. Due to the short half-life of ^{135}Te, the fission yield can be integrated with ^{135}I. This results in a cumulative fission yield of $\gamma_I = 0.065$ [11]

Because of the short half-life of tellurium-135, the Iodine can be considered as the primary fission product. This means the cumulative fission yield of ^{135}I can be used ($\gamma_I = 0.064$) [11]. The concentration of ^{135}Xe can be calculated adding the contributions of decay from ^{135}I, fission of ^{235}U and subtracting the decay to ^{135}Cs and the absorption of neutrons:

$$\frac{\mathrm{d}Xe(t)}{\mathrm{d}t} = \lambda_I I(t) + \gamma_X \Sigma_f \phi - \lambda_X Xe(t) - \sigma_{aX} Xe(t)\phi \tag{3.6}$$

This expression depends on $I(t)$ which is determined in the same way, using the production from fission and subtracting the decay to Xenon:

$$\frac{\mathrm{d}I(t)}{\mathrm{d}t} = \gamma_I \Sigma_f \phi - \lambda_I I(t) \tag{3.7}$$

In these expressions, λ is the decay constant, γ is the fission yield, Σ_f is the macroscopic fission cross section ($\Sigma = N\sigma$) and ϕ is the neutron flux.

3.2. Serpent burnup calculations

In this study a Monte Carlo based code for burnup calculations in nuclear reactors, Serpent, is used for extensive calculations. A short overview will follow about some of the physics behind this code, to get an idea of how it works.

3.2.1. Monte Carlo method

Monte Carlo is a computational method that is used for simulating many different types of complex physical and mathematical problems, such as situations with high uncertainties in the input or many coupled degrees of freedom. By repeatedly taking random samples, numerical results are collected that in a way can be interpreted and processed as the results of a physical measurement [6].

The reason Monte Carlo is used for the calculations in Serpent is that it is capable of calculating statistical estimates for all the reactions within the reactor, without actually solving for the exact flux distribution [7].

3.2.2. Neutron transport calculation

For calculating the behaviour of the neutrons inside the reactor, the movement of single neutrons is tracked through material regions of the geometry. Using statistical mathematics, a probability density function can be found for the free path lengths of the neutrons. However, this PDF is only statistically valid within one material. When the simulated neutron reaches a boundary in the geometry, its path is adjusted or re-sampled for the remaining distance to the next collision [7].

In order to calculate the distance to the closest approaching boundaries, the complete geometry needs to be build from simple geometrical objects that can be written in closed form.

3.2.3. Result estimates

The simulated 'events', such as the earlier described path lengths and surface crossings, but also absorption and scattering collisions, are all combined to form statistical estimates of physical quantities. This way, results can be collected. These results are printed into text files that can be processed using matlab, in order to create useful tables and figures. From these tables and figures the desired information can be obtained.

4

Numerical approach

As stated earlier, in section 1.2.3, this report continues with the code written by Elgin [2] and adjusted by van Egmond [12]. The code is based on a Serpent simulation of the tube and core geometry. For the complete specifics of this geometry and core input values in Serpent, see references. In the first step, the 12 sections of the loop are filled with a solution of uranyl nitrate. Every step the content is irradiated for 15 minutes. Serpent runs the burnup calculation and returns an output file with all present materials in each section and their current concentrations. Matlab converts this outputfile to an inputfile for the next step by moving the content of every section to the next and adding new salt to section 1. This process is repeated 15 times. After 12 steps, the salt that started in section 1 has passed through the complete loop. Now the content of section 12 has been irradiated for a complete cycle and the last three steps show that a steady state is established immediately after this event (figure 4.1). Since the results do not fluctuate after the cycle is completed, it can be concluded that these first steps do not influence the final concentration and can be neglected for long term calculations.

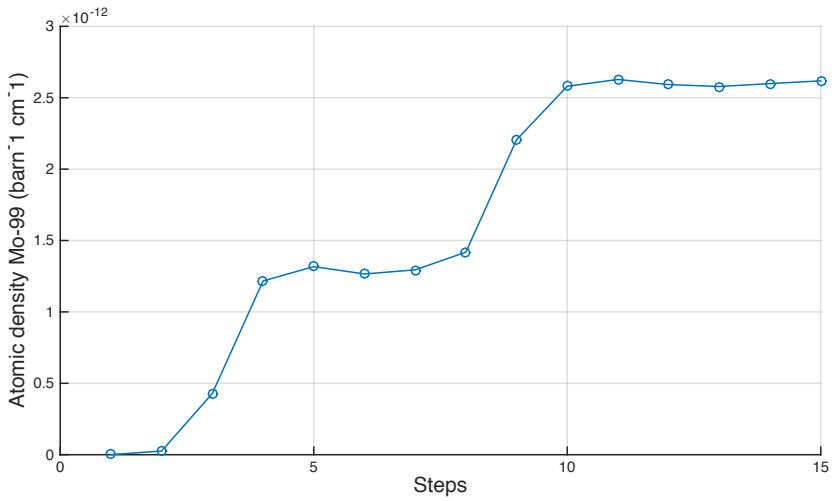

Figure 4.1: Molybdenum-99 concentration result in original code. After 12 steps the salt that initially started in section 1 reached section 12. From this moment the system is steady state.

It should be noted that Serpent generates a new seed for every separate step. This means a different set of random numbers is used for every Monte Carlo calculation. This way a mean of different possible outcomes is found as output, instead of only one example of a possible outcome.

In this report the code is adjusted to be able to investigate the long-term behaviour of the loop content.

4.1. Introducing recirculation of the salt

First the salt in the loop needs to be recirculated. In the old code new salt is added to section 1 after every step. Considering that only a fraction of the uranium is consumed every time the salt passes through the loop, it is not desirable to be adding new salt to the system. To solve this, an adjustment is made in the Matlab script. After every step, no new salt is added but the content of section 12 is moved to section 1 (figure 4.2). In addition the possibility is added to filter the ^{99}Mo or other materials from the salt before it re-enters section 1 (figure 4.3).

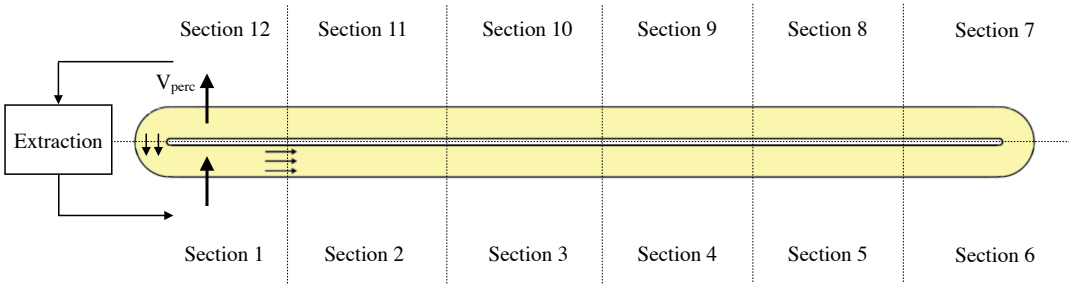

Figure 4.2: The loop, divided in 12 sections, with indicated extraction system. In section 12, a certain percentage of the total loop volume, V_{perc}, is tapped off. From this small flow all ^{99}Mo is extracted, and the resulting solution is fed back into section 1.

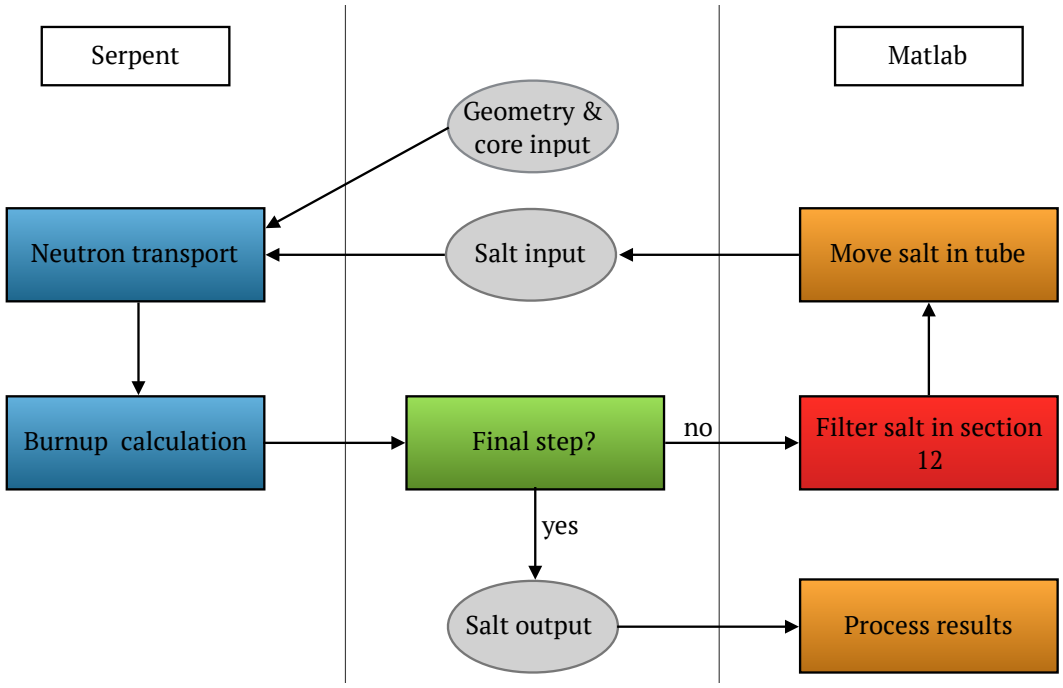

Figure 4.3: A schematic illustration of the adjusted code. In this code no new salt is added but the content of section 12 is filtered, as indicated in red, and fed back into section 1.

4.2. Increasing the irradiation time

The original code is only able to run a calculation of 15 steps. This relates to a total irradiation time of 3 hours. The code is easily converted into a loop where the amount of steps can be chosen as desired. The bigger problem is the time it will take to run the code. In the original code it takes about 3 hours to calculate an irradiation of 3 hours. To speed up the calculation, some adjustment are made.

To increase the speed, the accuracy of the calculation needs to be reduced. The population size of the neutrons is changed from 20.000 to 5000. The accuracy scales with $\sqrt{n}$, so reducing the population with a factor 4, which increases the speed by a factor 4, will only double the error.

Turning off the pcc option in Serpent, for predictor-corrector calculation, also increases the calculation speed. This method results in a more accurate estimation of isotopic changes during each burnup step. Because he transport cycle in repeated, the method increases the overall calculation time. This option is, however, maintained because the influence on the calculation speed is a lot smaller than the previously mentioned adjustment. For very long irradiation times it might be significant anyway, so further experiments on the accuracy influence of this option could be done.

After this adjustment, an irradiation time of approximately 5 days can be calculated overnight.

4.3. Processing the results

The final salt output from Serpent is retrieved in the form of a text file with all present materials and their densities. In the original code these files needed to be copied from the cluster to be able to process them. For a simulation of 15 steps this is no problem, but considering the size of the simulations in this report it is no longer possible. A matlab script is written to process the results, when they are still on the cluster, to a more compact matlab file that can be imported to a personal computer. This file still contains all information about the present materials.

When this compact file is imported, information can be extracted. Several matlab scripts are written to extract and process the information from the salt output.

5

Analytical calculations

Despite of the adjustments in section 4.2, it is not efficient to calculate the long-term behaviour of the loop content with Serpent. The results of different Serpent simulations can however be used to create a sufficiently accurate analytical model for the materials of interest. First, an expression for $U(t)$, the concentration of ^{235}U, is determined which is used to determine $Xe(t)$ and $Mo(t)$. This model can be used to make predictions for the behaviour after many years.

In the analytical model, the spacial dependence is neglected. The time of one circulation trough the tube is 3 hours. In this report the behaviour of the loop content after many years is predicted. Because the time of one circulation is not significant, the complete loop can be approximated as an ideally stirred tank.

5.1. Determining an analytical expression for the ^{235}U concentration

In section 3.1.5, an expression for the uranium-235 concentration is given (equation 3.4). This expression only contains the neutron flux ϕ through the tube and the neutron absorption cross section ^{235}U, σ_{aU}. The average flux is unknown and influences like the geometry of the system and the presence of Xenon-135 are not considered. To implement these factors in the expression, the Serpent results can be used. An estimation of the complete geometry, flux and salt composition can be bundled in one constant, α. When equation 3.4 is written as

$$\frac{\mathrm{d}U(t)}{\mathrm{d}t} = -\alpha U \tag{5.1}$$

the slope of the exponentially decreasing ^{235}U concentration in the Serpent results can be used to determine α.

When a value of α is found, the differential equation can be solved and an analytical expression of $U(t)$ is obtained for the longer term calculations. With this expression the equations for ^{135}Xe and ^{99}Mo can be determined.

5.2. Determining an analytical expression for the ^{135}Xe concentration

For the calculation of $Xe(t)$, the expressions mentioned in section 3.1.5 are used. In this section it is explained that the expression for $Xe(t)$ is determined by the decay of ^{135}I, the fission of ^{235}U, the decay to other nuclei and the absorption of neutrons. For the effective neutron flux in these equations, equations 3.4 and 5.1 are combined:

$$\phi = \frac{\alpha}{\sigma_{a,U}} \tag{5.2}$$

Implementing this in equation 3.7, the following expression for $I(t)$ is obtained.

$$\frac{\mathrm{d}I(t)}{\mathrm{d}t} = \gamma_I \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha U(t) - \lambda_I I(t) \tag{5.3}$$

This expression can be used to solve the final equation of $Xe(t)$:

$$\frac{\mathrm{d}Xe(t)}{\mathrm{d}t} = \lambda_I I(t) + \gamma_X \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha U(t) - \lambda_X Xe(t) - \sigma_{aX} Xe(t) \frac{\alpha}{\sigma_{a,U}} \tag{5.4}$$

5.3. Determining an analytical expression for the ^{99}Mo concentration

A similar approach can be used for $Mo(t)$. ^{99}Mo is mainly a decay product of several other fission products. Only a fraction of the ^{99}Mo is produced directly by fission. In figure 5.1 this process is illustrated, where the yields are extracted from the JEFF-3.1 fission yield library (via [8]) and the half-lifes from [3].

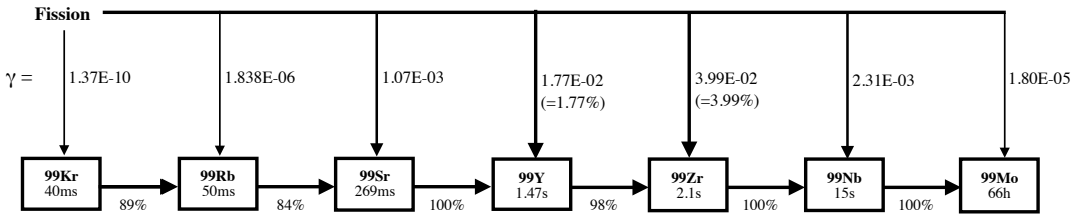

Figure 5.1: The process of fission and decay leading to ^{99}Mo with indicated fission yields and half-lives. It can be seen that ^{99}Y and ^{99}Zr are the most important sources of ^{99}Mo. However, the cumulative fission yield of ^{99}Mo, γ_{Mo} = 0.0613, is used since the half-lives of the intermediate nuclei are very short.

It can be seen from the independent fission yields, γ, of the intermediate fission products, that mainly the production of Yttrium-99 and Zirconium-99 contribute to the ^{99}Mo production. Together with Niobium-99 and Strontium-99 they give a cumulative fission yield of 0.0576. However, considering the short half-life of all intermediate fission products, these stages can be neglected and their yields merged. The total cumulative fission yield of ^{99}Mo, 0.0613 is used, instead of adding each contribution separately. For λ_{Mo}, the half-life of ^{99}Mo, which is 66 hours, is used.

Since a fraction of the salt will be tapped from the loop to extract the produced ^{99}Mo, another term will appear in the expression for $Mo(t)$. When looking at a time scale much bigger than the time of one circulation, the entire loop can be approximated as an ideally stirred tank with a small mass flow going out and no ^{99}Mo coming back in [1]. This results in

$$\frac{dMo(t)}{dt} = \gamma_{Mo} \Sigma_{f,U} \phi - \lambda_{Mo} Mo(t) - V_{perc} Mo(t) \tag{5.5}$$

where V_{perc} is the fraction of the total volume of the loop that is being tapped and filtered. Again implementing the expression for ϕ, this will become

$$\frac{dMo(t)}{dt} = \gamma_{Mo} \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha U(t) - \lambda_{Mo} Mo(t) - V_{perc} Mo(t). \tag{5.6}$$

[1] Assuming the extraction columns are ideal. Further research is to be done on this subject.

6 Results

6.1. The adjusted code

The results of the adjustments to the code stated in chapter 4 are illustrated in figure 6.1. The result of the ^{99}Mo concentration from the original code, that can only calculate 15 steps, is plotted together with the result of the adjusted code where the loop content is recirculated, the ^{99}Mo is filtered and the neutron population is reduced to 5000. It can be seen that the recirculation of the salt does not influence the concentration of ^{99}Mo.

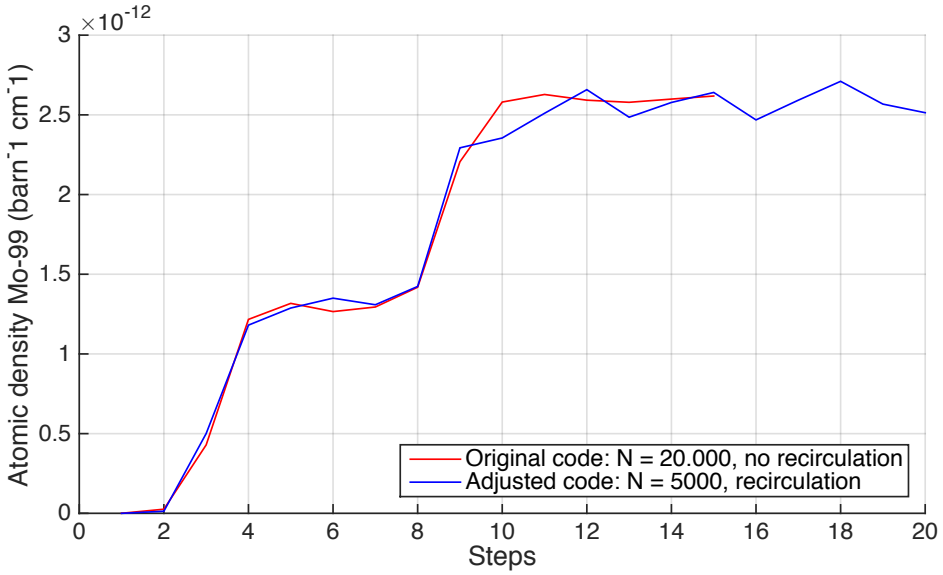

Figure 6.1: The results of the ^{99}Mo concentration in the original code and the adjusted code. The recirculation does not influence the results. It can be seen that a lower neutron population was used in the adjusted code, decreasing the accuracy.

Before continuing with a neutron population of 5000, the influence on the results is determined. In figure 6.2 both populations are plotted for 50 steps. It is clear the results from the smaller population is fluctuating more, indicating more uncertainty, but the average concentration stays the same. This accuracy will be sufficient for the long-term calculations in this report because only the average converged concentration is used.

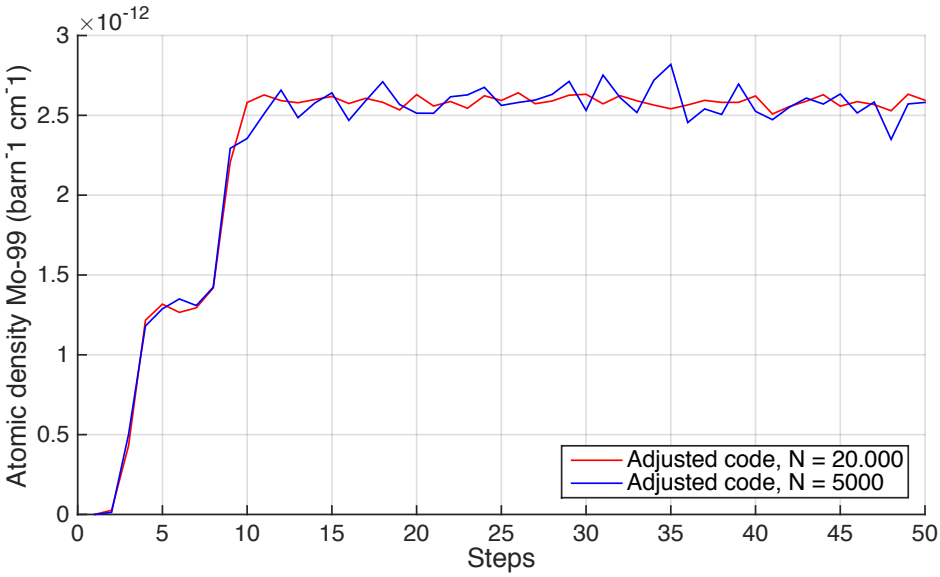

Figure 6.2: Molybdenum-99 concentration results for different neutron populations. It can be seen that the lower neutron population gives a more fluctuating result. This will however not be of significant influence in the long-term simulations in this report, since the average concentration is not effected.

6.2. Analytical results

To solve the analytical expressions from chapter 5, the coefficient α needs to be determined. The coefficient can not be calculated directly by using a fitting tool. Because the irradiation time of the Serpent simulation is very small, relative to the time scale of the analytical solution, fitting the Serpent output would result in a linear equation. Since from the Serpent result only the initial slope can be determined, α is calculated by solving equation 5.1 for $t = 0$. The slope of $U(t)$ at $t = 0$ can be determined from the Serpent results using the cftool function in matlab. Evaluating

$$\frac{dU(t=0)}{dt} = -\alpha U_0 \tag{6.1}$$

returns a value of $\alpha = 3.1673 \cdot 10^{-10}\text{barn}^{-1}\text{cm}^{-1}\text{sec}^{-1}$. To get an explicit expression for $U(t)$, the differential equation 5.1 can be solved to obtain

$$U(t) = U_0 \, e^{-\alpha t}. \tag{6.2}$$

With this result, the expression for $I(t)$ and $Xe(t)$(equations 5.3 and 5.4) can be solved:

$$I(t) = \frac{\gamma_I \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha \, U_0}{\lambda_I - \alpha} \left(e^{-\alpha t} - e^{-\lambda_I t} \right) \tag{6.3}$$

$$Xe(t) = \left(\frac{I\lambda_I e^{t(K-\alpha)}}{K-\alpha} - \frac{I\lambda_I e^{t(K-\lambda_I)}}{K-\lambda_I} + \frac{\gamma_X U e^{t(K-\alpha)}}{K-\alpha} - \frac{I\lambda_I}{K-\alpha} + \frac{I\lambda_I}{K-\lambda_I} - \frac{U\gamma_X}{K-\alpha} \right) e^{-Kt} \tag{6.4}$$

where the following constants are substituted for readability:

$$I = \frac{\gamma_I \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha \, U_0}{\lambda_I - \alpha}$$

$$U = \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha U_0$$

$$K = \lambda_X + \sigma_{a,X} \frac{\alpha}{\sigma_{a,U}}$$

Also $Mo(t)$ can be solved.

$$Mo(t) = \frac{\gamma_{Mo} \frac{\sigma_{f,U}}{\sigma_{a,U}} \alpha \, U_0}{(\lambda_{Mo} + V_{perc}) - \alpha} \left(e^{-\alpha t} - e^{-(\lambda_{Mo} + V_{perc})t} \right) \tag{6.5}$$

6.3. Validation of the analytical model

6.3.1. Validation of U(t)

To compare the result of $U(t)$ to the Serpent results, six calculations were done in Serpent. The consumption of ^{235}U is relatively low, leading to a slow and gradual decrease taking many years. Since it takes a lot of time to simulate a few days in Serpent, a single calculation would not generate enough information to create a useful image for the validation of $U(t)$. For this reason, six smaller calculations were done, each starting with only a certain percentage of the original ^{235}U concentration.

The six serpent calculations give an impression of the slope of $U(t)$, each after a different amount of time. The last five calculations, with reduced ^{235}U concentration, are simulations with an irradiation time of 5 days. The first calculation, with 100% ^{235}U, is a simulation with an irradiation time of 30 days. In this calculation, all fission products that converge within 30 days, such as ^{135}Xe, have reached their final concentration. Therefore the output of this calculation is used as an input for the other 5 calculations where the ^{235}U consumption after a longer period is estimated. The only adjustment to this output is the ^{235}U concentration. This value is reduced to respectively 90%, 80%, 70%, 50% and 10% of the initial concentration.

In figure 6.3, the analytical solution is illustrated together with the Serpent results. The analytical expression is used to determine the location of the five Serpent results on the x-axis. This means that the Serpent results are moved along the x-axis manually to the point in time where they meet with the analytical result. By zooming in on the Serpent results there slope can now be compared to $U(t)$.

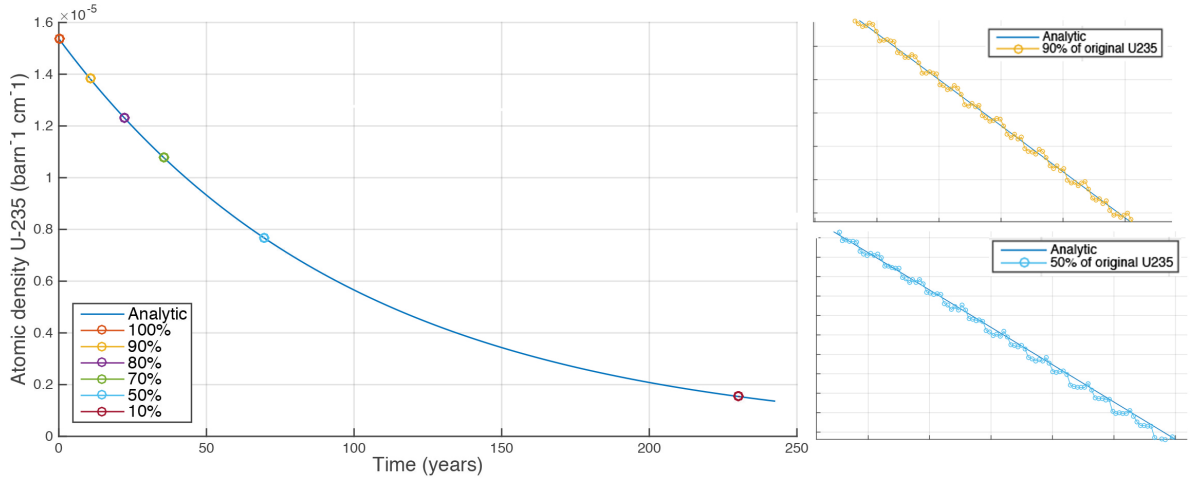

Figure 6.3: Analytically determined ^{235}U compared to the Serpent results for different percentages of the original uranium concentration. The Serpent results are moved along the x-axis manually so their slopes can be compared to the analytical result. Left: Overview with all Serpent results. Right: Zoomed in plots of 90% and 50%. It can be seen that the fit is more accurate for the high concentrations of ^{235}U.

For the high concentrations of ^{235}U, it can be seen that the slopes are very similar to the analytical result. At the lower concentrations however, the slope of the Serpent results appear to be slightly steeper than the analytical result. Since the input of the last 5 Serpent calculations is the output from the first calculation, where an irradiation time of 30 days is simulated, any development in the loop content that still changes after 30 days is not accounted for in the Serpent calculations.

6.3.2. Validation of I(t), Xe(t) and Mo(t)

In figures 6.4 and 6.5, the analytical results of $I(t)$ and $Xe(t)$ are compared to Serpent. It is clear that in both cases the analytical values are higher than the Serpent results. $I(t)$, indicated in red in figure 6.4, converges at a value that is 6.5% higher than the Serpent result. $Xe(t)$, indicated in red in figure 6.5, converges at a value that is 13% higher than the Serpent result, twice the deviation of $I(t)$.

In figure 6.4, also an improved expression of $I(t)$ is indicated. It can be seen that this function converges at the same value as the Serpent result. This function is obtained by multiplying the original expression with 0.935, which was found empirically. Using this adjusted expression of $I(t)$, a more accurate expression of $Xe(t)$ is obtained. In figure 6.5, it can however be seen that, when the adjusted expression for $I(t)$ is used to calculate $Xe(t)$, the expression still converges at a value that is 6.5% higher than the Serpent result, a devia-

tion similar to the deviation of $I(t)$. From this result it can be seen that the origin of this error is present in both the expression for $I(t)$ and $Xe(t)$ and that the error is accumulated in the expression for $Xe(t)$.

For the comparison of $Mo(t)$, a situation is simulated where the ^{99}Mo is not extracted because the extraction methods of the Serpent simulation and the analytical model are not similar. Simulating the build-up of ^{99}Mo without extraction, a comparison can be made. Also $Mo(t)$ turns out to converge at a higher value than in Serpent (figure 6.6), having a deviation of 5%.

When the consumption of uranium is modelled accurately, the geometry is completely accounted for because the fission of uranium is, however indirectly, the only cause of the production of ^{99}Mo. Also the build-up of most of the fission products should be captured within this model, since for example ^{135}Xe converges already after a few days. It is investigated whether slight changes in α can lead to big effects on the results. However, when α is decreased with 5% the converged value of $Mo(t)$ also decreases with only 5%. This means that when α is decreased with 5%, the $Mo(t)$ expression will correspond with the Serpent result, but the fit of $U(t)$ will not. This means the error is not caused by an uncertainty in α.

If the error is not caused by an uncertainty in α, the source of the deviation can either be in the fact that the disappearance of ^{235}U is not only the result of neutron absorption, or in the simplifications of the analytical differential equations. Since the half-life of ^{235}U is $7.04 \cdot 10^8$ years, this first possibility is probably not the source. In the simplifications of the model however, a systematic deviation of 5% is also higher than expected. In the expressions for $I(t)$ and $Mo(t)$, the neutron absorption is neglected. This is not expected to affect the results with 5% since the absorption cross-section of ^{135}I and ^{99}Mo are relatively small. Also the same deviation of 5% is found in the expression of $Xe(t)$, where the absorption is not neglected, so the neutron absorption is not the source of the error. The neglect of intermediate fission products with short half-lives can also not possibly cause this deviation, since these half-lives all are below a few seconds. This is not a significant period in the calculations of behaviour after many years.

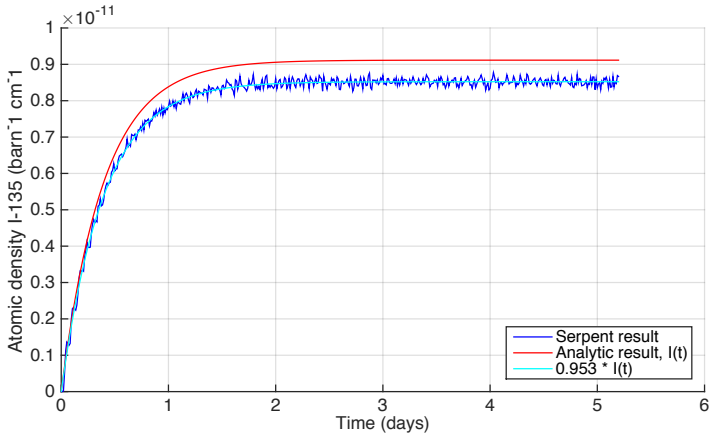

Figure 6.4: The analytically determined ^{135}I is compared to the Serpent result. It can be seen that the analytical result converges higher then the result from Serpent. Also an adjusted expression for $I(t)$ is given. This expression is empirically aligned with the result from Serpent by multiplication with 0.935. This expression is used to obtain an expression for $Xe(t)$ without accumulated deviation.

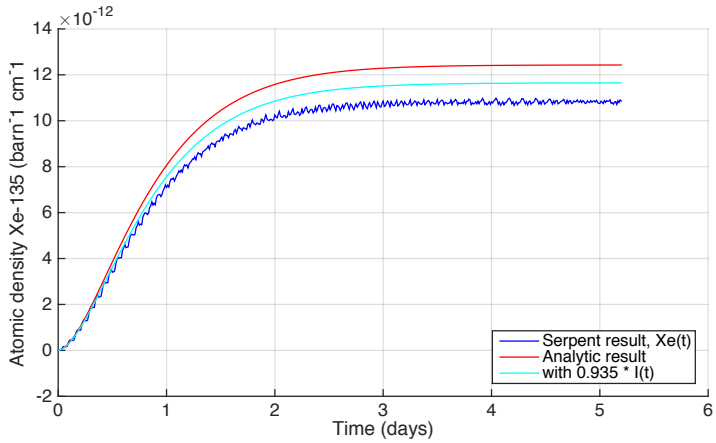

Figure 6.5: The analytically determined ^{135}Xe is compared to the Serpent result. Also the expression that was obtained using te adjusted $I(t)$ is illustrated. Since the deviation of the original expression is twice the deviation of the adjusted value, it can be seen that $I(t)$ and $Xe(t)$ have an equal, systematic deviation.

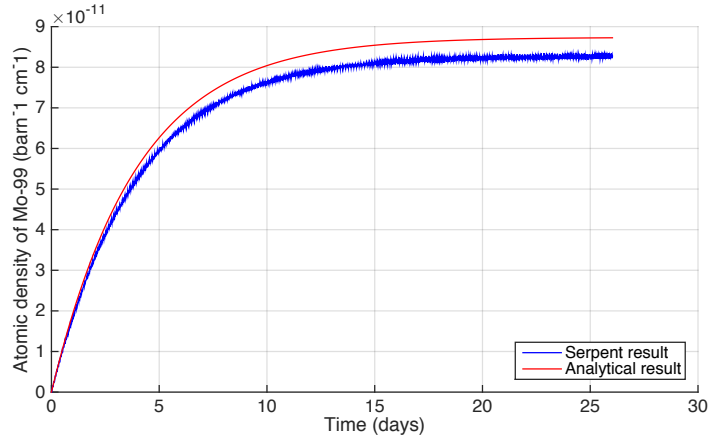

Figure 6.6: The analytically determined ^{99}Mo concentration is compared to the Serpent result. Also this analytical results converges to higher values then the result from Serpent.

6.4. ^{99}Mo production loss over time

When a small fraction of the loop content is tapped and filtered, the ^{99}Mo concentration will converge at a certain value, dependent on the tapped flow V_{perc} (figure 6.7). V_{perc} is the percentage of the total loop volume that is tapped off.

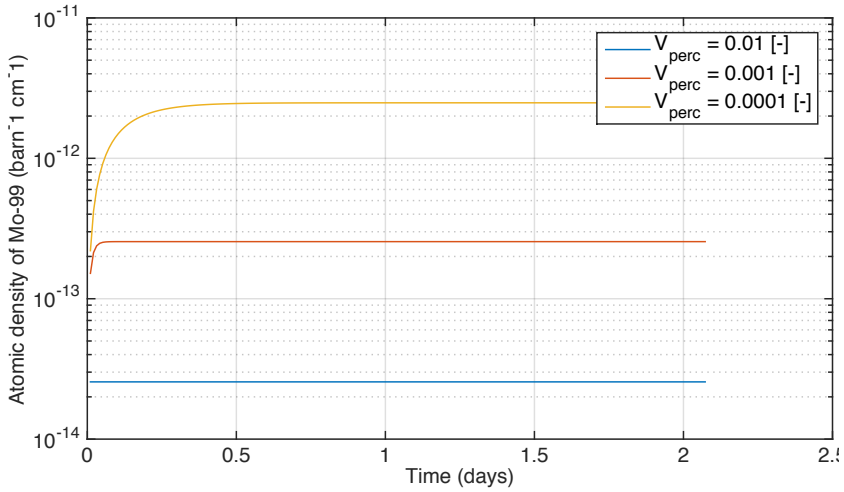

Figure 6.7: The ^{99}Mo concentration in the outflow for different values of V_{perc}. The concentration is higher for low values of V_{perc}, but the product of V_{perc} and $Mo(t)$ is approximately the same for every choice of V_{perc}.

The production $P(t)$ of ^{99}Mo however, does not significantly depend on V_{pers}, since

$$P(t) = V_{perc} \cdot Mo(t) \tag{6.6}$$

This approximately results in a value of $P(t) = 2.5 \cdot 10^{-16}\,\text{barn}^{-1}\text{cm}^{-1}\text{sec}^{-1}$ for every choice of V_{perc}. However, ^{99}Mo decays to ^{99}Tc with a half life of 66 hours, so when a bigger flow is filtered, less molybdenum will be lost by decay to ^{99}Tc. To make a meaningful estimation of the desired flow, the separation process needs to be taken into consideration. Further research should be done on this subject.

As the uranium in the solution is consumed over time and the amount of fission products builds up, the production of ^{99}Mo decreases. In this report a salt concentration of 30 g/L is used for the simulations. The production that can be obtained from this concentration is estimated to satisfy 0.2% of the worldwide ^{99}Mo demand. As mentioned earlier, in section 1.2.1, further research has to be done on solving the problem of heat production in the loop. When a new design is created with less heat production and better cooling, it will be possible to use a higher concentration of uranyl nitrate, resulting in different production values. Therefore, in this report, the production is normalized with respect to the initial production, to illustrate only the relative decrease of the isotope production. In figure 6.8, the normalized production is illustrated. It can be seen that after 22 years for example, 80% of the original production still is available. Since $U(t)$ decreases as an exponential function, this normalized result should be a valid approximation for every choice of the initial uranyl concentration.

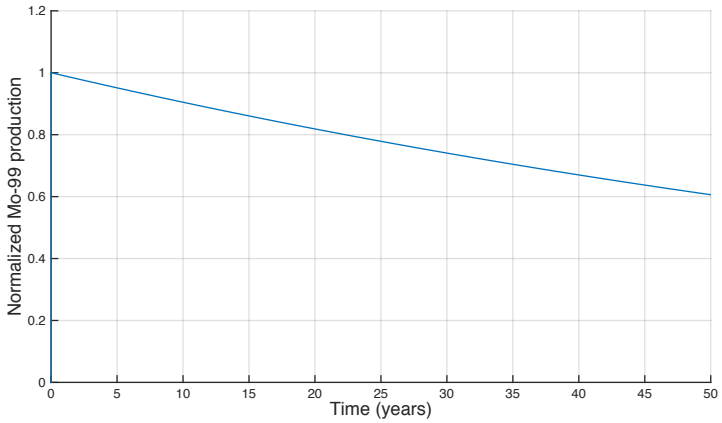

Figure 6.8: The decrease of the ^{99}Mo concentration. The decease is normalized because the actual uranyl concentration in the salt is not yet determined. Changing this concentration will influence the production, but not the decrease of the production. It can be seen that for example after 22 years, 80 % of the original production is left.

6.5. Influence of filtering ^{135}Xe

To investigate the influence of the ^{135}Xe production in the loop, a simulation is done in Serpent where all $Xe(t)$ and $I(t)$ is filtered from the system. The present ^{135}Xe captures a part of the neutrons that would have lead to fission of uranium. In figure 6.9 it can indeed be seen that slightly more uranium is consumed when ^{135}Xe is filtered from the loop. This leads to a slightly bigger production of ^{99}Mo. The new α that can be obtained from this steeper slope is $\alpha = 3.1712 \cdot 10^{-10}\,\text{barn}^{-1}\text{cm}^{-1}\text{sec}^{-1}$, a fraction higher than the original value. This change will extend the salt durability with a few days, which is not significant for the long-term.

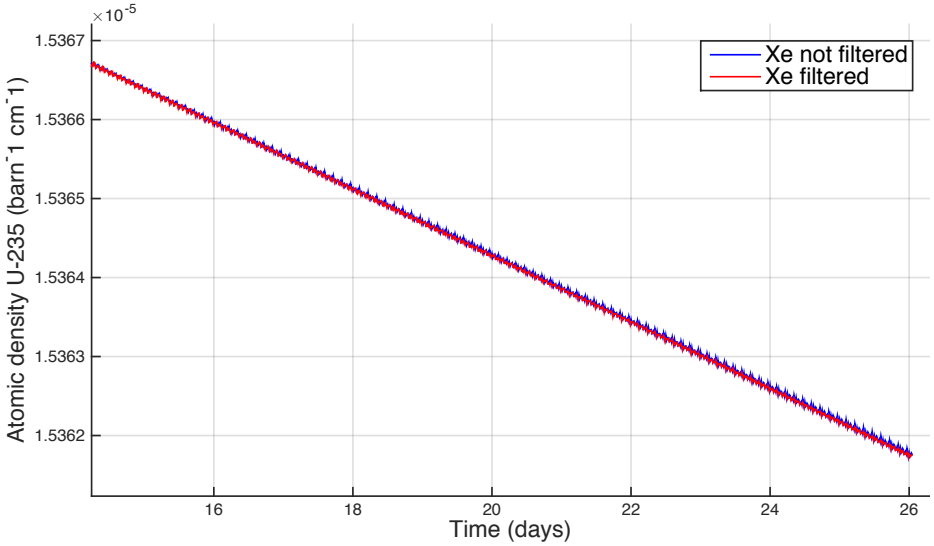

Figure 6.9: The ^{235}U concentration in the loop with and without filtering of ^{135}Xe. When ^{135}Xe is filtered the slope is slightly steeper. This means slightly more uranium is consumed and thereby more ^{99}Mo is produced. However the influence of this effect on the isotope production is not significant.

7

Conclusions and discussion

This report studies a segment of the research into implementing a loop, filled with uranyl nitrate, near the core of the Hoger Onderwijs Reactor in Delft to produce ^{99}Mo. After recycling the salt for a certain time, a part of the uranium will be consumed and several fission products are building up in the loop.These long-term effects will have a negative influence on the production of ^{99}Mo. The goal of this report is to study the durability of the salt and predict the time it can be recirculated before the ^{99}Mo production becomes too low and the salt needs replacement.

Using Serpent, several simulations are done for irradiation periods of 5 to 30 days. These results are used to create an analytical model of materials of interest in the loop. With this model the production of ^{99}Mo after several years can be predicted.

Using the same Serpent code and analytical model, also the influence of ^{135}Xe on the production of ^{99}Mo is investigated.

7.1. Durability of the salt

Using the analytical model an expression for the production of ^{99}Mo was obtained. Because the actual concentration of uranyl nitrate in the loop is not yet determined, the output is normalized with respect to the initial production. Suppose a minimum of 80% of the original production is desired, the loop would last 22 years. When after this time a higher production is wanted, the solution should be replaced or replenished.

7.2. Influence of ^{135}Xe on the production of ^{99}Mo

To obtain an indication of the influence of ^{135}Xe on the isotope production in the loop, a Serpent simulation is done where ^{135}Xe and its parent ^{135}I are extracted from the solution. With the output a new expression of the ^{99}Mo production is calculated. The effects of this experiment are however not significant.

7.3. Discussion

In this report a simple analytical model is created of several materials inside the ^{99}Mo research loop. The loop is a more complex system then is accounted for in this model. Only the most important decay, fission and absorption reactions are accounted for.

In reality, and in the Serpent simulations, the exact geometry of the system, the gradual build-up of many fission products and the decay, fission and absorption of less important nuclei also play a role. It is attempted to capture most of these complex factors, that can not be accounted for in a simple analytical model, into one coefficient, α. This number is obtained by analysing the slope of $U(t)$ in a Serpent simulation of 30 days of irradiation. This means all influences on the consumption of uranium that occur within 30 days are accounted for.

However the source of the deviation of 5% is not found, the results are considered accurate enough for the purposes of this study. This deviation of 5% in $Mo(t)$ leads to a deviation is the durability prediction of approximately one year.

7.4. Further research

Before the Mo-loop can be implemented, further research on several segments of the loop need to be done.

Different recirculation methods can be investigated. For example, it can be studied if it is favourable to continuously add a small amount of uranyl nitrate to the loop. This way it can be prevented that the complete loop content needs to be replaced.

Also, a solution needs to be found for the heat production in the loop. In this report a uranyl concentration of 30 g/L was used, because in the current design higher concentrations would lead to temperatures above 100°C, causing the salt to boil. However a higher concentration of around 300 g/L is desired to obtain a substantial production of ^{99}Mo. Only if a new design is created with lower heat production and better heat transfer, this can be achieved.

In addition, the extraction method of ^{99}Mo, and possibly ^{135}I and ^{135}Xe, can be studied. With more knowledge on this subject, decisions can be made considering the velocity of the salt through the tube and the size of the tapped flow.

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