Thermodynamic Study of Sequential Chlorination for Spent Fuel Partitioning

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This study examined the efficacy of various chlorinating agents in partitioning light water reactor spent fuel, with the aim of optimizing the chlorination process. Through thermodynamic equilibrium calculations, we assessed the outcomes of employing $MgCl_2$, NH_4Cl, and Cl_2 as chlorinating agents. A comparison was drawn between using a single agent and a sequential approach involving all three agents ($MgCl_2$, NH_4Cl, and Cl_2). Following heat treatment, the utilization of $MgCl_2$ as the sole chlorinating agent resulted in a moderate separation. Specifically, this method yielded a solid separation with 96.9% mass retention, 31.7% radioactivity, and 44.2% decay heat, relative to the initial spent fuel. In contrast, the sequential application of the chlorinating agents following heat treatment led to a final solid separation characterized by 93.1% mass retention, 5.1% radioactivity, and 15.4% decay heat, relative to the original spent fuel. The findings underscore the potential effectiveness of a sequential chlorination strategy for partitioning spent fuel. This approach holds promise as a standalone technique or as a complementary process alongside other partitioning processes such as pyroprocessing. Overall, our findings contribute to the advancement of spent fuel management strategies.

Keywords: Thermodynamic calculation, Equilibrium composition, Sequential chlorination, Spent fuel, Partitioning

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1. Introduction

The high radioactivity and decay heat of spent fuel comes mostly from a few elements such as Pu, Am, Cm, Cs, Sr, Ba, Y, Eu, and Kr. These elements can be classified into groups with similar chemical behavior, and their physical properties can also vary by group. For example, ^{239}Pu, which belongs to the actinide group, has a half-life of 24,100 years, while ^{137}Cs and ^{90}Sr, which belongs to the alkali and alkaline earth metals group, have significantly shorter half-lives of 30 years and 29 years, respectively. Pyroprocessing has been developed in conjunction with fast reactors to separate spent fuel into groups, and then store cesium and strontium for about 300 years to reduce radioactivity and decay heat, and recycle plutonium along with americium and curium as fuel to convert them into short-lived nuclides while generating electricity [1-5].

Apart from recovering and recycling zirconium from the cladding of light water reactor spent fuel through chlorination [6], chlorination can also be employed to partitioning of spent fuel components. Efforts are underway to develop chlorination processes using $MgCl_2$, NH_4Cl, Cl_2, $ZrCl_4$, CCl_4, etc. as chlorinating agents [7-12]. Recently, Deep Borehole Disposal has emerged as a promising disposal method [13-14]. If the chlorination products are separated according to their radioactivity and decay heat, and then processed into a solid waste form with a height and diameter suitable for Deep Borehole Disposal, the disposal efficiency can be greatly improved while reducing the burden of large-diameter drilling for Deep Borehole Disposal. Pyroprocessing pretreatment technique such as oxide electrowinning have been sought that can reduce the burden of pyroprocessing by reducing the amount of material to be processed in pyroprocessing [15]. If the chlorination process is combined with pyroprocessing as a pretreatment process, it can be expected to substantially reduce the amount of material that needs to undergo pyroprocessing.

In this study, the efficiency of $MgCl_2$ and NH_4Cl chlorinating agents, which have recently attracted attention, was compared with the basic chlorinating agent, Cl_2, through thermodynamic equilibrium calculations. Additionally, this study evaluated the enhanced partitioning effects achieved when chlorination agents are sequentially applied, as compared to using a single chlorinating agent. The findings of this study are expected to contribute to the optimization of the chlorination process and expand its applications.

2. Methodology

In this study, a light water reactor spent fuel with an initial enrichment of 4.5wt% ^{235}U, a release burnup of 55 GW/MtU, and 10 years of cooling was chosen as the reference spent fuel. The main 50 nuclides present in the spent fuel were analyzed, and the amount of spent fuel was 10,003 kg on an elemental basis. Spent fuel components can exist in various oxidation states depending on the degree of burnup [16]. Since it is difficult to perform equilibrium calculations considering all the various oxidation states, equilibrium calculations were performed using the chemical forms shown in Table 1 as a starting point, and the mass, radioactivity, and decay heat were expressed accordingly.

The volatile and semi-volatile components of the spent fuel can be separated from the spent fuel through heat treatment [17]. Through heat treatment in an oxidizing atmosphere, the UO_2 in the spent fuel is further oxidized increasing its volume and transforming the spent fuel into a powder form, which can increase the reaction rate of the subsequent chlorination process. In this study, it is assumed that group 1 (H, Rb, Cs) and some other elements (Kr, Xe, C, Sb, Br, I, Te, Se) are completely volatilized and separated from the solid product during the heat treatment process performed at 1,400°C. As shown in Tables 2 and 3, it is assumed that 100% of the UO_2 is converted to U_3O_8 and 100% of the Tc is converted to Tc_2O_7 and volatilized during the heat treatment process. As a result, the chlorination process used the spent fuel components shown in Table 2 as inputs. Table 2 shows that the actinide compounds constitute the majority of the

Table 1. Reference spent nuclear fuel: initial U enrichment of 4.5wt%, discharge burnup of 55 GW/MtU, 10 yrs cooling

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	Ac_2O_3, ThO_2, PaO_2, UO_2, NpO_2, PuO_2, AmO_2, CmO_2	10,698.2	1,347.8	6.0
Alkali & Alkaline earth	Rb_2O, Cs_2O, SrO, BaO	103.0	3,720.4	8.8
Rare earth	Y_2O_3, La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3, Pm_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3	200.7	1,152.9	5.8
Volatile	Kr, Xe, H, CO_2, Sb, Br, I, TeO_2, SeO_2	113.5	98.0	0.15
Etc.	Fe, Ni, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn	203.3	17.3	0.081
Sum		11,318.7	6,336.4	20.8

Table 2. Mass, radioactivity, and decay heat of solid products after heat treatment

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	Ac_2O_3, ThO_2, PaO_2, U_3O_8, NpO_2, PuO_2, AmO_2, CmO_2	11,114.6	1,347.8	6.0
Alkali & Alkaline earth	SrO, BaO	48.6	2,238.9	6.2
Rare earth	Y_2O_3, La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3, Pm_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3	200.7	1,152.9	5.8
Etc.	Fe, Ni, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn	190.8	17.1	0.081
Sum		11,554.7	4,756.7	18.1

Table 3. Mass, radioactivity, and decay heat of vapor products after heat treatment

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	-	0.0	0.0	0.0
Alkali & Alkaline earth	Rb_2O, Cs_2O	54.4	1,481.5	2.6
Rare earth	-	0.0	0.0	0.0
Volatile	Kr, Xe, H_2, CO_2, Sb, Br, I_2, TeO_2, SeO_2	113.5	98.0	0.15
Etc.	Tc_2O_7	12.5	0.2	0.0001
Sum		180.4	1,579.7	2.8

Table 4. Mass, radioactivity, and decay heat of oxides and oxychlorides products after heat treatment and chlorination by $MgCl_2$

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	ThO_2, $ThOCl_2$, PaO_2, $PaCl_2O$, U_3O_8, UO_2Cl, UO_2Cl_2, U_4O_9, UO_2, $(UO_2)_2Cl_3$, U_3O_7, $UOCl_2$, $UOCl_3$, NpO_2, $NpOCl_2$, PuO_2, $PuOCl$, $AmOCl$, AmO_2, $CmOCl$, CmO_2	11,267.4	1,312.1	5.9
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	Y_2O_3, $YOCl$, $LaOCl$, $CeOCl$, $PrOCl$, $NdOCl$, Pm_2O_3, $SmOCl$, $EuOCl$, $GdOCl$, Tb_2O_3, $TbOCl$, Dy_2O_3, $DyOCl$, Ho_2O_3, $HoOCl$, Er_2O_3, $ErOCl$, Tm_2O_3, $TmOCl$, Yb_2O_3, $YbOCl$, Lu_2O_3, $LuOCl$	104.7	678.0	3.2
Etc.	Fe, Ni, Zr, Nb, Mo, Rh, Ru, Pd, Ag, Cd, In, Sn	189.9	17.1	0.08
Sum		11,562.0	2,007.2	9.2

Table 5. Mass, radioactivity, and decay heat of chlorides products after heat treatment and chlorination by $MgCl_2$

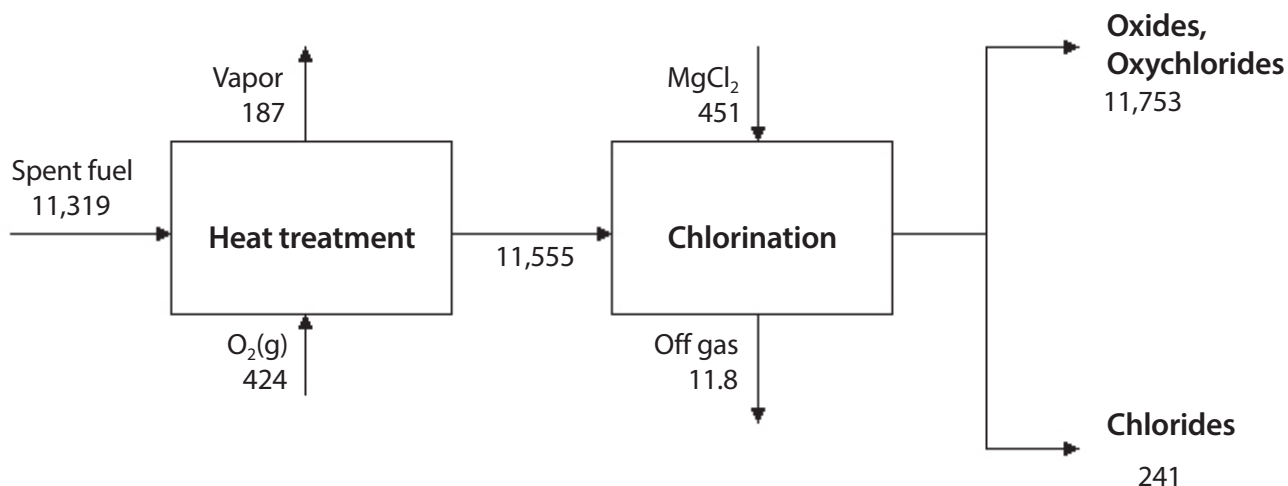|		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	$AcCl_3$, $ThCl_4$, $PaCl_3$, $PaCl_5$, $NpCl_4$, $NpCl_3$, $PuCl_3$, $AmCl_3$, $CmCl_3$	5.2	35.6	0.1
Alkali & Alkaline earth	$SrCl_2$, $BaCl_2$	68.5	2,238.8	6.2
Rare earth	YCl_3, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $PmCl_3$, $SmCl_3$, $EuCl_3$, $EuCl_2$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, $YbCl_2$, $LuCl_3$	166.3	474.2	2.5
Etc.	$ZrCl$, $AgCl$, $InCl$	1.3	0.0004	0.0
Sum		241.3	2,748.6	8.8

solid product's mass after heat treatment (96.19%), while the radioactivity is dominated by the alkaline earth metal compounds (SrO, BaO) (47.07%).

Thermodynamic equilibrium compositions and process flow of the chlorination reaction were evaluated using HSC Chemistry Software [18]. The HSC-Equilibrium module of the software employs the Gibbs energy minimization method to calculate equilibrium product amounts in isothermal and isobaric conditions. Additionally, the HSC-Sim module of the software was used for the simulation of chemical reactions encompassing both the heat treatment unit and the chlorination units.

3. Results and Discussion

3.1 Chlorination by Using a Single Chlorination Agent

Among the products of chlorination by $MgCl_2$, the oxides and oxychloride are shown in Table 4, and the chlorides products are shown in Table 5. $MgCl_2$ chlorination was assumed to proceed by immersing the solid product from the heat treatment in molten $MgCl_2$ at 800°C. The inputs to the equilibrium calculation were 1 mol of spent fuel reactants and 5 mol of $MgCl_2$. It was assumed that, in the molten

Fig. 1. Mass flow (kg) of heat treatment and chlorination by using $MgCl_2$.

Table 6. Mass, radioactivity, and decay heat of oxides and oxychlorides products after heat treatment and chlorination by NH_4Cl

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	ThO_2, $ThOCl_2$, $PaCl_2O$, UO_2, NpO_2, $PuOCl$, $AmOCl$, $CmOCl$	10,601.6	450.0	3.3
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	$YOCl$, $LaOCl$, $CeOCl$, $PrOCl$, $NdOCl$, $SmOCl$, $EuOCl$, $GdOCl$, $TbOCl$, $DyOCl$, $HoOCl$, $ErOCl$, $TmOCl$, $YbOCl$, $LuOCl$	33.4	774.8	4.3
Etc.	Mo, Rh, Ru, Pd, Ag, Sn	128.7	17.0	0.08
Sum		10,763.7	1,241.8	7.7

salt, the oxides and oxychlorides precipitated as 100% solids, while the chlorides remained in the liquid phase. Therefore, in the mass flow, the oxide and oxychloride are in the same stream, while the chloride is in a separate stream. Using $MgCl_2$, alkaline earth metal oxides are completely converted to chlorides, while actinide oxides and transition and noble metals are only converted to chlorides in relatively small amounts. This suggests that $MgCl_2$ is an effective chlorinating agent for separating alkaline earth metals from actinides, transition and noble metals. Notably, when $MgCl_2$ is used as a chlorinating agent, various uranium

oxides and uranium oxychlorides are produced, as shown in Table 4. Fig. 1 illustrates the mass flow of the heat treatment and $MgCl_2$ chlorination process. The spent fuel mass of 10,003 kg on an elemental basis is 11,319 kg on an oxide basis, and the solid products mass of the heat treatment increases to 11,555 kg, mainly due to the weight gain in the conversion of UO_2 to U_3O_8. Chlorination requires 451 kg of $MgCl_2$, with $Cl_2(g)$ and $O_2(g)$ as off-gases. When $MgCl_2$ is used as the chlorinating agent, the oxides and oxychlorides stream is accompanied by 191 kg of MgO produced by the reaction of $MgCl_2$ with oxides.

Table 7. Mass, radioactivity, and decay heat of chlorides products after heat treatment and chlorination by NH_4Cl

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	$AcCl_3$, $ThCl_4$, $PaCl_3$, $NpCl_3$, $PuCl_3$, $AmCl_3$, $CmCl_3$	126.5	897.8	2.7
Alkali & Alkaline earth	$SrCl_2$, $BaCl_2$	68.5	2,238.9	6.2
Rare earth	YCl_3, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $PmCl_3$, $SmCl_3$, $EuCl_3$, $EuCl_2$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_2$, $YbCl_3$, $LuCl_3$	257.7	378.1	1.5
Etc.	$FeCl_2$, $NiCl_2$, $ZrCl_4$, $NbCl_{2.67}$, $NbCl_{3.13}$, $NbCl_{2.33}$, $NbCl_3$, $NbCl_2$, $NbCl_4$, $CdCl_2$, $InCl_3$, $InCl_2$, $InCl$	156.9	0.07	0.00001
Sum		609.6	3,514.9	10.4
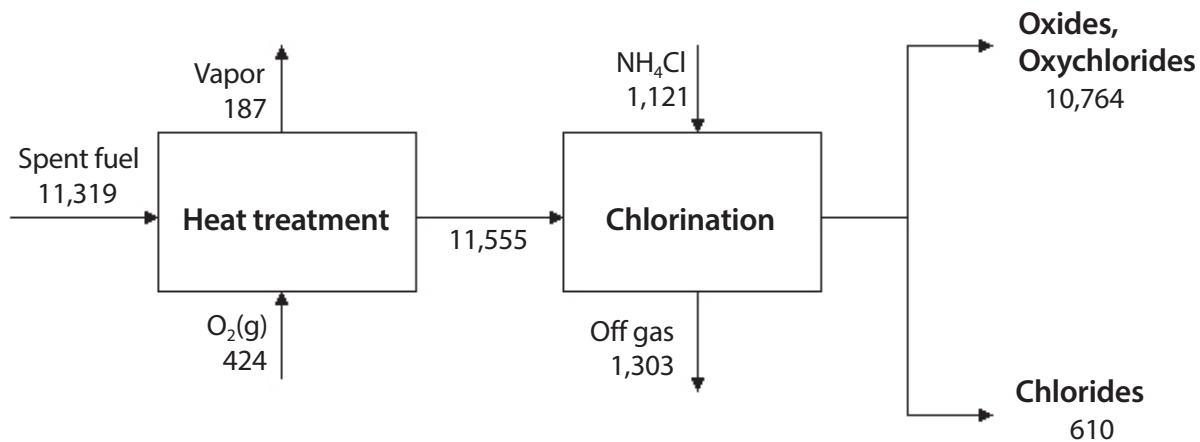
Fig. 2. Mass flow (kg) of heat treatment and chlorination by using NH_4Cl.

Among the products of chlorination by NH_4Cl, the oxides and oxychloride are shown in Table 6, and the chlorides products are shown in Table 7. NH_4Cl chlorination was assumed to proceed by reacting the solid product from the heat treatment with NH_4Cl at 370°C in a sealed container. The inputs to the equilibrium calculation were 1 mole of spent fuel reactants and 10 moles of NH_4Cl. After the reaction, the chlorination output was assumed to be immersed in LiCl-KCl molten salt at 500°C resulting in the precipitation of the oxides and oxychlorides as 100% solids, while the chlorides remained in the liquid phase. It was assumed that LiCl-KCl molten salt has no chlorinating effect. When NH_4Cl is used as a chlorinating agent, NH_4Cl is decomposed, and $H_2(g)$ and $Cl_2(g)$ participate in the reaction. Therefore, chlorination by NH_4Cl is carried out in a reducing atmosphere. Unlike $MgCl_2$ chlorination, NH_4Cl chlorination only produces UO_2 for uranium and PuOCl and $PuCl_3$ for plutonium, suggesting relatively simple separation of plutonium from uranium. Identical to $MgCl_2$ chlorination, NH_4Cl chlorination completely converts alkaline earth metal oxides to chlorides. Fig. 2 shows the mass flow of the heat treatment and NH_4Cl chlorination process. For chlorination, 1,121 kg of NH_4Cl is required, and $Cl_2(g)$, $H_2O(g)$, $H_2(g)$, and $N_2(g)$ are generated as off-gases. The mass of chlorides produced by NH_4Cl chlorination is 610 kg, surpassing the chlorides mass obtained from $MgCl_2$

Table 8. Mass, radioactivity, and decay heat of oxides and oxychlorides products after heat treatment and chlorination by Cl_2

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	ThO_2, $ThOCl_2$, $PaCl_2O$, UO_2Cl_2, UO_3, NpO_2, PuO_2, $AmOCl$, $CmOCl$	11,639.0	1,320.5	5.1
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	$YOCl$, $LaOCl$, CeO_2, $Pr_{12}O_{22}$, $NdOCl$, $SmOCl$, $EuOCl$, $GdOCl$, $TbOCl$, $DyOCl$, $HoOCl$, $ErOCl$, $TmOCl$, $YbOCl$, $LuOCl$	75.5	939.5	5.2
Etc.	-	0.0	0.0	0.0
Sum		11,714.5	2,260.0	10.3

Table 9. Mass, radioactivity, and decay heat of chlorides products after heat treatment and chlorination by Cl_2

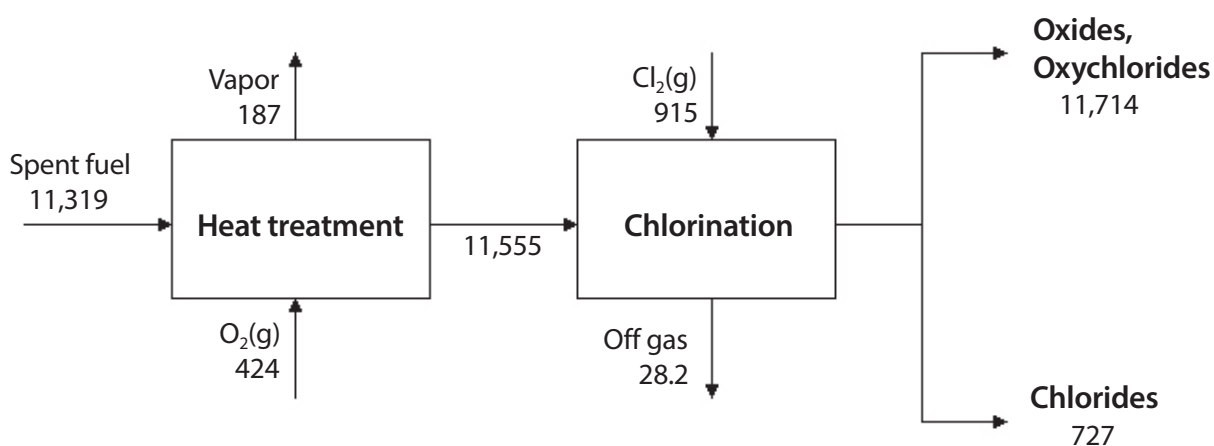|		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	$AcCl_3$, $AmCl_3$, $CmCl_3$	12.7	27.6	0.9
Alkali & Alkaline earth	$SrCl_2$, $BaCl_2$	68.5	2,238.8	6.2
Rare earth	YCl_3, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $PmCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, $LuCl_3$	191.9	210.3	0.6
Etc.	$FeCl_3$, $FeCl_2$, $NiCl_2$, $ZrCl_4$, $NbCl_5$, $MoCl_5$, $MoCl_4$, $RuCl_3$, $RhCl_3$, $PdCl_2$, $AgCl$, $CdCl_2$, $InCl_3$, $SnCl_2$	453.9	17.1	0.08
Sum		727.0	2,493.8	7.8

Fig. 3. Mass flow (kg) of heat treatment and chlorination by using Cl_2.

chlorination (241 kg), indicating a relatively stronger chlorination ability of NH_4Cl.

Among the products of chlorination by Cl_2, the oxides and oxychloride are shown in Table 8, and the chlorides products are shown in Table 9. Cl_2 chlorination was set to react $Cl_2(g)$ gas with the solid product from the heat treatment at 100℃. The inputs to the equilibrium calculation were 1 mol of spent fuel reactant and 5 mol of $Cl_2(g)$. After the reaction, the chlorination output was assumed to be immersed in LiCl-KCl molten salt at 500℃ resulting in the precipitation of the oxides and oxychlorides as 100% solids, while the chlorides remained in the liquid phase. Identical to $MgCl_2$ and NH_4Cl chlorination, Cl_2 chlorination completely converts alkaline earth metal oxides to chlorides. Notably, Cl_2 chlorination has the ability to convert 100% of the metals to chlorides distinguishing it from other chlorination processes. Consequently, Cl_2 chlorination is an effective chlorination method for separating metals from oxides and oxychlorides. Fig. 3 shows the mass flow of the heat treatment and Cl_2 chlorination process. The chlorination process necessitates 915 kg of $Cl_2(g)$ and $O_2(g)$ is generated as an off-gas. Although Cl_2 chlorination chlorinates actinide elements to a lesser extent than NH_4Cl chlorination, the complete conversion of metals to chlorides results in chlorides mass of 727 kg in Cl_2 chlorination, surpassing the chlorides mass obtained from NH_4Cl chlorination, which was 610 kg.

Table 10. Mass, radioactivity, and decay heat of oxides and oxychlorides products after heat treatment and chlorination by $MgCl_2$ and NH_4Cl

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	ThO_2, $ThOCl_2$, $PaCl_2O$, UO_2, $UOCl_2$, NpO_2, $NpOCl_2$, $PuOCl$, $AmOCl$, $CmOCl$	10,570.9	112.1	2.0
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	$YOCl$, $LaOCl$, $CeOCl$, P_2OCl, $NdOCl$, $SmOCl$, $GdOCl$, $TbOCl$, $DyOCl$, $HoOCl$, $ErOCl$, $TmOCl$, $YbOCl$, $LuOCl$	9.1	241.2	1.3
Etc.	Mo, Rh, Ru, Pd, Ag, Sn	128.7	17.0	0.08
Sum		10,708.7	370.3	3.4

Table 11. Mass, radioactivity, and decay heat of chlorides products after heat treatment and chlorination by $MgCl_2$ and NH_4Cl

|		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	$ThCl_4$, $PaCl_3$, UCl_3, UCl_4, $NpCl_3$, $PuCl_3$, $AmCl_3$, $CmCl_3$	167.0	1,199.9	4.0
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	YCl_3, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $PmCl_3$, $SmCl_3$, $EuCl_2$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, $YbCl_2$, $LuCl_3$	123.6	436.6	1.9
Etc.	$FeCl_2$, $NiCl_2$, $ZrCl_4$, $NbCl_{2.67}$, $NbCl_{3.13}$, $NbCl_{2.33}$, $NbCl_3$, $NbCl_2$, $NbCl_4$, $CdCl_2$, $InCl_3$, $InCl_2$, $InCl$	155.4	0.07	0.00001
Sum		446.0	1,636.6	5.9
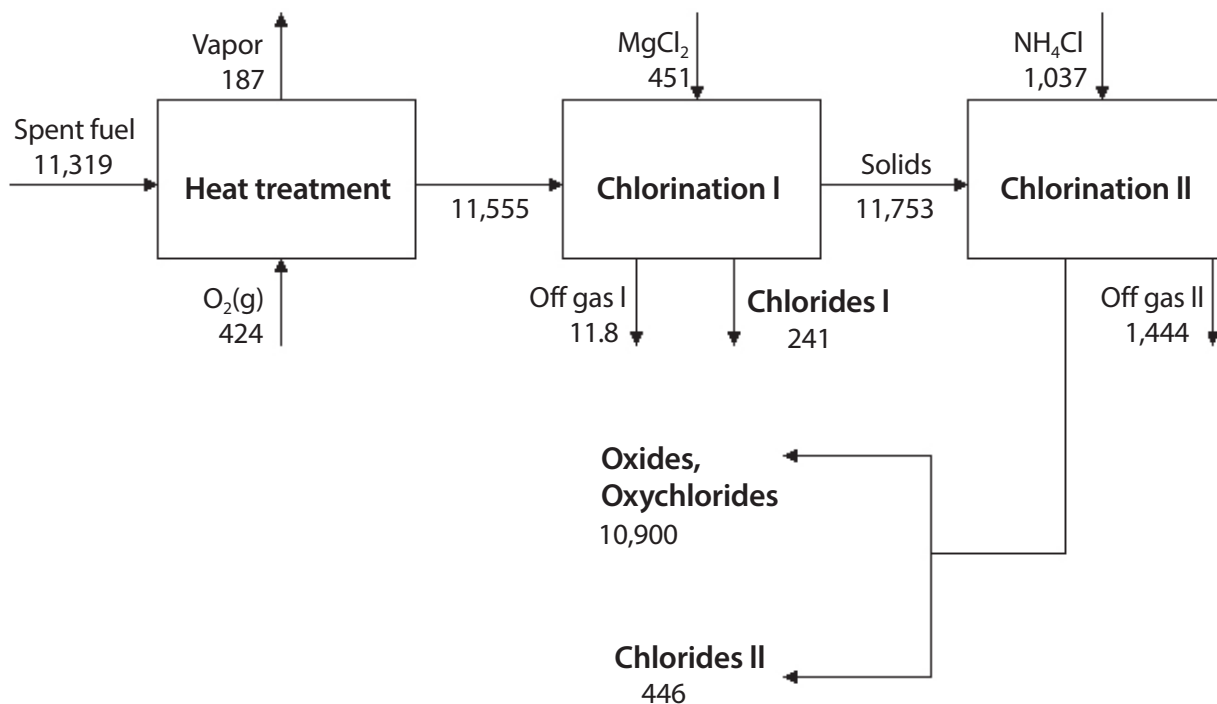
Fig. 4. Mass flow (kg) of heat treatment and chlorination by using MgCl$_2$ and NH$_4$Cl.

3.2 Sequential Chlorination

Additional NH$_4$Cl chlorination of oxides and oxychlorides produced from MgCl$_2$ chlorination was expected to further enhance the selective separation of highly radioactive actinide elements, rare earths, transition metals, and noble metals from actinide oxides composed primarily of uranium. Among the products of sequential application of MgCl$_2$ and NH$_4$Cl, the oxides and oxychloride are shown in Table 10, and the chlorides products are shown in Table 11. As with the use of MgCl$_2$ as a single chlorinating agent, the oxides and oxychlorides stream of sequential chlorination contains 191 kg of MgO produced by the reaction of MgCl$_2$ with oxides. Compared to the single chlorination agents of MgCl$_2$ and NH$_4$Cl, the masses of oxide and oxychloride in the sequential chlorination process are 92.6% and 99.5%, respectively. However, the radioactivity levels are only 18.4% and 29.8%, and the decay heat is only 36.8% and 44.0%, respectively. This indicates that sequential

chlorination can produce a stream with lower radioactivity and heat per unit mass compared to using a single chlorinating agent alone. Fig. 4 illustrates the mass flow when heat treatment, MgCl$_2$ chlorination, and NH$_4$Cl chlorination are performed sequentially. The total chloride amount resulting from the sequential chlorination of MgCl$_2$ and NH$_4$Cl is 651 kg, surpassing the 241 kg of chloride from MgCl$_2$ chlorination and 610 kg of chloride from NH$_4$Cl chlorination, indirectly indicating the additional chlorination achieved through sequential processes.

Due to Cl$_2$'s capability to completely separate metals from actinide oxides, Cl$_2$ chlorination was employed in conjunction with the oxide and oxychloride produced obtained from sequential MgCl$_2$ and NH$_4$Cl chlorination. Table 12 presents the oxide and oxychloride products resulting from the sequential application of MgCl$_2$, NH$_4$Cl, and Cl$_2$, while Table 13 displays the chloride products. The mass of the oxide and oxychloride products in the sequential chlorination process involving MgCl$_2$, NH$_4$Cl, and Cl$_2$

Table 12. Mass, radioactivity, and decay heat of oxides and oxychlorides products after heat treatment and chlorination by $MgCl_2$, NH_4Cl, and Cl_2

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	ThO_2, $ThOCl_2$, $PaCl_2O$, UO_2Cl_2, $UOCl_3$, NpO_2, $NpOCl_2$, PuO_2, $AmOCl$, AmO_2, $CmOCl$	13,325.9	82.9	1.9
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	$YOCl$, $LaOCl$, CeO_2, $Pr_{12}O_{22}$, $NdOCl$, $SmOCl$, $EuOCl$, $GdOCl$, $TbOCl$, TbO_2, $DyOCl$, $HoOCl$, Ho_2O_3, $ErOCl$, $TmOCl$, $YbOCl$, $LuOCl$	9.1	241.2	1.3
Etc.	-	0.0	0.0	0.0
Sum		13,335.0	324.1	3.2

Table 13. Mass, radioactivity, and decay heat of chlorides products after heat treatment and chlorination by $MgCl_2$, NH_4Cl, and Cl_2

		Mass (kg)	Radioactivity (kCi)	Decay heat (kW)
Actinide	UCl_4, UCl_5, UCl_6, $NpCl_4$, $NpCl_5$, $PuCl_3$, $PuCl_4$, $AmCl_3$	3.9	29.2	0.06
Alkali & Alkaline earth	-	0.0	0.0	0.0
Rare earth	$CeCl_3$, $PrCl_3$, $TbCl_3$, $HoCl_3$	0.0	0.01	0.0
Etc.	$MoCl_5$, $MoCl_4$, $RuCl_3$, $RhCl_3$, $PdCl_2$, $AgCl$, $SnCl_2$	301.7	17.0	0.08
Sum		305.6	46.2	0.14

is 124.5% compared to sequential chlorination involving $MgCl_2$ and NH_4Cl, whereas the radioactivity is 87.5% and the decay heat is 94.7%. This implies that each additional chlorination step in the sequential process leads to a solid product stream with lower radioactivity and decay heat per unit mass. In the case of sequential $MgCl_2$ and NH_4Cl chlorination, the uranium in the oxides and oxychlorides stream exists as UO_2 and $UOCl_2$, respectively. However, in sequential $MgCl_2$, NH_4Cl, and Cl_2 chlorination, the uranium in the oxides and oxychlorides stream exists as $UOCl_2$ and $UOCl_3$, resulting in a higher mass of oxide and oxychloride compared to $MgCl_2$ and NH_4Cl sequential chlorination. Fig. 5 illustrates the mass flow when heat treatment, $MgCl_2$, NH_4Cl, and Cl_2 chlorination are performed sequentially. The total chloride amount resulting from the sequential chlorination process involving $MgCl_2$, NH_4Cl, and Cl_2 is

993 kg, exceeding the total chloride amount obtained from sequential $MgCl_2$ and NH_4Cl chlorination (651 kg), indirectly indicating the progressive nature of chlorination as additional chlorination steps are implemented.

3.3 Comparison of Chlorination Effects

Table 14 presents the mass, radioactivity, and decay heat of the final solid products obtained through heat treatment and chlorination, allowing for a comparison of the effectiveness of the various chlorination processes examined in this study. Among the single chlorinating agents, NH_4Cl chlorination demonstrates the highest efficiency in separating materials of high radioactive and decay heat from the uranium-dominant solid product. When combining heat treatment with $MgCl_2$ chlorination, the resulting final solid
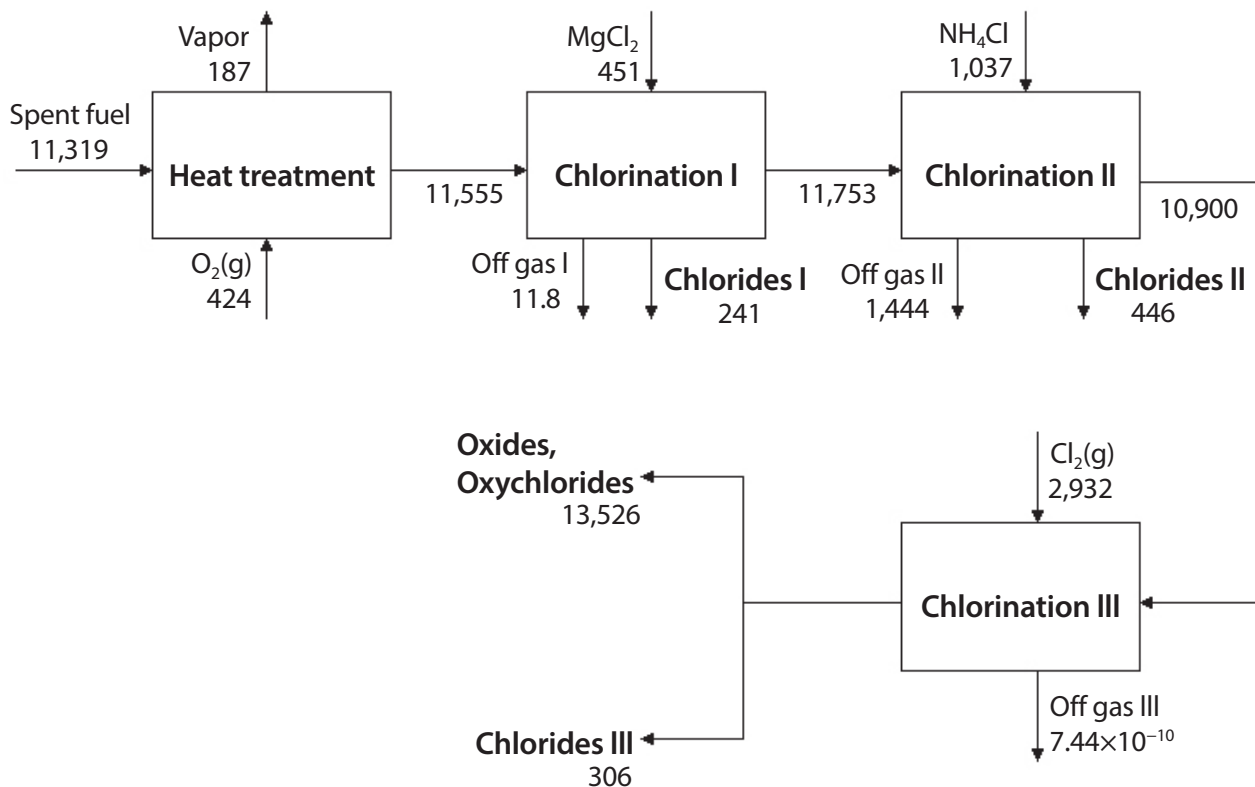
Fig. 5. Mass flow (kg) of heat treatment and chlorination by using $MgCl_2$, NH_4Cl, and Cl_2.

Table 14. Comparison of mass (elemental basis), radioactivity, and decay heat of solid products after heat treatment and sequential chlorination

	Input	Heat treatment	Chlorination ($MgCl_2$)	Chlorination (NH_4Cl)	Chlorination (Cl_2)	Chlorination ($MgCl_2 \rightarrow NH_4Cl$)	Chlorination ($MgCl_2 \rightarrow NH_4Cl \rightarrow Cl_2$)
Mass (kg)	10,002.7	9,835.7	9,694.1	9,495.0	9,482.9	9,445.4	9,313.6
Mass /Input mass (%)	100	98.3	96.9	94.9	94.8	94.4	93.1
Radioactivity (kCi)	6,336.4	4,756.7	2,007.2	1,241.8	2,260.0	370.3	324.1
Radioactivity /Input radioactivity (%)	100	75.1	31.7	19.6	35.7	5.8	5.1
Decay heat (kW)	20.8	18.1	9.2	7.7	10.3	3.4	3.2
Decay heat /Input decay heat (%)	100	87.0	44.2	37.0	49.5	16.3	15.4

Table 15. Comparison of radioactivity (kCi) distribution through heat treatment and sequential chlorination

		Chlorination ($MgCl_2$)	Chlorination ($MgCl_2 \rightarrow NH_4Cl$)	Chlorination ($MgCl_2 \rightarrow NH_4Cl \rightarrow Cl_2$)
Actinide	Oxides/Oxychlorides	1,312.1	112.1	82.9
	Chloride I	35.8	35.8	35.8
	Chloride II	0.0	1,199.9	1,199.9
	Chloride III	0.0	0.0	29.2
Alkali & Alkaline earth	Oxides/Oxychlorides	0.0	0.0	0.0
	Vapor from heat treatment	1,481.5	1,481.5	1,481.5
	Chloride I	2,238.9	2,238.9	2,238.9
	Chloride II	0.0	0.0	0.0
	Chloride III	0.0	0.0	0.0
Rare earth	Oxides/Oxychlorides	678.0	241.2	241.2
	Chloride I	475.0	475.0	475.0
	Chloride II	0.0	436.6	436.6
	Chloride III	0.0	0.0	0.01
Volatile	Solid product from heat treatment	0.0	0.0	0.0
	Vapor from heat treatment	98.0	98.0	98.0
Etc.	Oxides/Oxychlorides	17.1	17.0	0.0
	Vapor from heat treatment	0.2	0.2	0.2
	Chloride I	0.0004	0.0004	0.0004
	Chloride II	0.0	0.07	0.07
	Chloride III	0.0	0.0	17.0

product accounts for 96.9%, 31.7%, and 44.2% of the mass (elemental basis), radioactivity, and decay heat of the introduced spent fuel, respectively. On the other hand, combining heat treatment with sequential $MgCl_2$, NH_4Cl, and Cl_2 chlorination yields a final solid product representing 93.1%, 5.1%, and 15.4% of the mass (elemental basis), radioactivity, and decay heat of the introduced spent fuel, respectively. These results indicate the effectiveness of sequential chlorination in partitioning spent fuel, although the additional costs and operational challenges associated with multiple chlorination processes must be taken into accounts.

Table 15 shows how the radioactivity of each nuclide group is distributed to the mass flow as the chlorination progresses. Sequential chlorination proves capable of enhancing the purity of the uranium-dominant solid product while directing a majority of the highly radioactive actinide material towards the chlorides stream. Alkali and alkaline earth metals can be separated into vapor and chlorides streams. However, the chlorination-based separation of alkali and alkaline earth metals is a low-level separation accompanied by certain rare earths, transition metals, and precious metals. Notably, rare earths are present in both the oxides and oxychlorides stream and the chlorides stream, making it difficult to selective separation of them by chlorination.

The chlorides stream resulting from sequential chlorination exhibits a higher proportion of high radioactive material by mass compared to the initial spent fuel. Utilizing this chlorides stream as input for more selective separation

processes such as pyroprocessing is expected to alleviate the processing burden, while precipitating and solidifying the chlorides enables the production of a solid waste form suitable for Deep Borehole Disposal in terms of diameter and height. This approach may eliminate the need to drill large-diameter boreholes, addressing one of the technical challenges of Deep Borehole Disposal.

4. Conclusion

Thermodynamic equilibrium calculations were employed to determine the chemical forms and quantities of 50 major nuclides in light water reactor spent fuel, which were transformed into oxides, oxychlorides, and chlorides through chlorination. Simulations were conducted to obtain mass flows for heat treatment and chlorination processes. Sequential chlorination using $MgCl_2$, NH_4Cl, and Cl_2 demonstrated enhanced selectivity in group separation of the spent fuel, surpassing the capabilities of a single chlorinating agent. These findings substantiate the potential of sequential chlorination as a pretreatment technology for disposal, in conjunction with Deep Borehole Disposal, or as a pretreatment technology to reduce the amount of material that needs to be processed in pyroprocessing.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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