Original Article

Effect of oxygen containing compounds in uranium tetrafluoride on its non-adiabatic calciothermic reduction characteristics

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ABSTRACT

Uranium ingot is produced by metallothermic reduction of uranium tetrafluoride using magnesium or calcium as reductant. Presence of oxygen containing compounds viz. uranyl fluoride and uranium oxide in the starting uranium fluoride has a significant effect on the firing time, final temperature of the charge, slag-metal separation and hence the metal recovery. As reported in the literature, the maximum tolerable limit for uranyl fluoride in the UF_4 is 2.5 wt% and limit for uranium oxide content is in the range 2–3 wt%. No theoretical or experimental basis is available till date for these limits. Analyses have been carried out in this study to understand the effect of UO_2F_2 concentration in the starting fluoride on the final temperature of the products and thus the reduction characteristics. UF_4 having uranyl fluoride concentration, less than as well as more than 2.5 wt%, have been investigated. Thermodynamic calculations have been carried out to arrive at a general expression for the final temperature attained by the products during calciothermic reduction of UF_4. Finally, an upper limit for the oxygen containing impurities has been estimated using the $CaO-CaF_2$ phase diagram.

1. Introduction

Uranium forms the backbone of the nuclear energy programmes worldwide. Uranium metal is required to produce various uranium alloys viz. UAl_3, U_3Si_2; which are then used to fabricate fuel for LEU (Low Enriched Uranium) based high flux research reactors [1–5]. Uranium metal is also required to produce LEU based irradiation targets for Mo^{99} radioisotope production, for radiopharmaceutical manufacturing [3–8]. LEU poses restrictions on its quantity due to criticality considerations, and hence its preparation (by metallothermic reduction of uranium fluoride) needs to be carried out at smaller scale (few kilograms scale) [4,5].

Apart from processing of LEU fuel, other requirements for which small scale uranium ingot preparation by reduction of UF_4 is required include, reduction trials for quality check of the UF_4 synthesized by some new processes e.g. direct reduction of UF_6, hydrofluorination of UO_2 prepared by dry route from UF_6 etc. The quality of the UF_4 synthesized by these novel processes needs to be assessed, and this can be done by examining the uranium recovery in the ingot by performing reduction of this fluoride at smaller scale. Presence of oxygen containing impurities in the fluoride might hamper the ingot recovery [9].

At plant scale (few hundred kilograms), magnesiothermic reduction of uranium tetrafluoride is the universally adopted method for the production of uranium ingot [9–11]. Calcium is also used for this purpose, and in fact, offers greater heat of the reaction, so that better slag-metal separation can be obtained [9,11,12]. However, due to the high cost and higher requirement of calcium per unit mass as compared to magnesium, it is not employed as a reducing agent for plant scale processes. Moreover, in plant scale processes, the system is nearly under adiabatic conditions and hence approximately whole of the reaction heat is utilised in raising the temperature of the charge [9,11]. Hence, the heat of reaction offered by magnesium is sufficient to result in efficient slag—metal separation. When the size of the system is small (few kilograms), non-adiabatic conditions prevail, as heat losses occur due to increased surface area to volume ratio [4,5,13]. Hence, calcium is preferred as a reductant in such cases to compensate the heat losses.
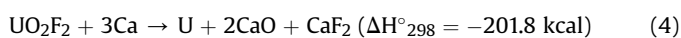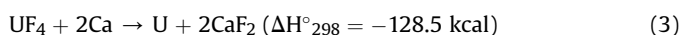
Literature reports suggest that the presence of oxygen containing compounds in the starting fluoride have a significant effect on the firing time, final temperature of the charge, the slag-metal separation and hence the metal recovery [9,11]. Similar effects are encountered in reduction of UF_4 both by Mg and Ca. UF_4 is

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produced by hydrofluorination of UO_2 using anhydrous HF at 450 °C (723 K) for 2 h [9,14,15]. UO_2 used for hydrofluorination is prepared by reduction of UO_3 with ammonia [9,11]. The UF_4 so produced generally contains small amounts of water soluble content i.e. uranyl fluoride (UO_2F_2) and ammonium oxalate insolubles (AOI) in the form of mixed oxides (UO_x). Higher UO_2F_2 content in UF_4 is the result of higher UO_3 content in the uranium oxide undergoing hydrofluorination ($UO_2 + 4HF \rightarrow UF_4 + 2H_2O$; $UO_3 + 2HF \rightarrow UO_2F_2 + H_2O$). The higher UO_3 content in UF_4 results from incomplete reduction of UO_3. Higher UO_2 content in the UF_4 is the result of incomplete hydrofluorination [9]. In addition, the green salt (UF_4) also contains moisture and free acidity in the form of HF. The best metal yields (about 97%) are achieved using green salt (UF_4) of about 98% assay with a 1% water soluble content (UO_2F_2) and 1% AOI content (UO_x), i.e. the mixed oxides. However, with a water soluble content of 2.5% and AOI content of 2.5% in the starting UF_4, yields of the order of about 95% are obtained. The rest of the uranium is present partly as beads and small plates and partly as finely divided and unreduced material in the slag [9,11,13].

Uranyl fluoride, heated in the presence of moisture, hydrolyzes to uranium trioxide and hydrogen fluoride. The HF formed results in a prolonged firing time, due to formation of fluoride film over magnesium (or calcium) [9,11]. The heat of reaction of uranyl fluoride with Ca and Mg is even higher than the heat of reaction of UF_4 with these reductants (see Reactions 1 to 4). Both these effects of the presence of UO_2F_2, i.e. prolonged firing time and additional heat of reaction, are desirable in non adiabatic condition. The prolonged firing time allows more sensible heat to the charge and suppresses the occurrence of premature reactions. The additional heat of reaction contributes to the fluidity of the metal-slag mixture at the time of the reaction; resulting in better slag-metal separation. The heat of reactions (against the reactions 1 to 4) are taken from Ref. [9], and verified by calculating the same using enthalpy data from Ref. [16].

$$UF_4 + 2\ Mg \rightarrow U + 2MgF_2\ (\Delta H°_{298} = -83.5\ \text{kcal}) \tag{1}$$

$$UO_2F_2 + 3\ Mg \rightarrow U + 2MgO + MgF_2\ (\Delta H°_{298} = -159.1\ \text{kcal}) \tag{2}$$

$$UF_4 + 2Ca \rightarrow U + 2CaF_2\ (\Delta H°_{298} = -128.5\ \text{kcal}) \tag{3}$$

$$UO_2F_2 + 3Ca \rightarrow U + 2CaO + CaF_2\ (\Delta H°_{298} = -201.8\ \text{kcal}) \tag{4}$$
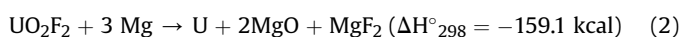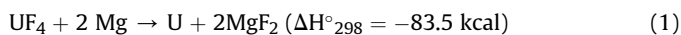
The effects mentioned above are most beneficial when UO_2F_2 content in the starting UF_4 is between 0.5 and 2.5%, as reported in literature [9,11]. For plant scale processes (nearly adiabatic condition), the practical limit of UO_2F_2 content is 2.5%, and experience has shown that when this limit is exceeded, the long firing time which allows more sensible heat to be transferred to the system, combined with the increased heat of reaction and thus a faster reaction rate, make it difficult to contain the reaction under production conditions [9]. However, in relatively smaller scale systems (non-adiabatic condition), where the batch size is few kilograms, clear slag-metal separation does not occur, owing to unproductive heat loss in reactor, structural materials etc. In such cases, the green salt with water-soluble content (UO_2F_2 percent) greater than 2.5% could be beneficial.

In our study, for smaller (few kilograms) scale, we employed calcium as reducing agent and several experimental trials of reduction of UF_4 samples having UO_2F_2 concentration both greater than as well as less than 2.5 wt% were performed. Analyses have been carried out in this study to understand the effect of UO_2F_2 concentration less than 2.5 wt%, as well as greater than 2.5 wt% on the final temperature of the products. The effect of UO_2F_2 greater than 2.5 wt% has not been reported in literature till date.

Thermodynamic calculations have been carried out to arrive at a general expression for the final temperature attained by the products during calciothermic reduction of UF_4. This temperature has been evaluated for five different experiments of calciothermic reduction of UF_4, where the content of UO_2F_2 and unconverted oxides were the variables. Finally, an upper limit for these oxygen containing compounds has been estimated using the CaO–CaF_2 phase diagram [17].

2. Materials and methods

2.1. Details of the raw materials

Five different samples of uranium tetrafluoride with varying UO_2F_2 and mixed oxide content were used for the present study. As explained in Section 1, higher UO_2F_2 content is the result of higher UO_3 content in the uranium oxide undergoing hydrofluorination and higher UO_3 content results from incomplete reduction of UO_3. Higher UO_2 content in the UF_4 is the result of incomplete hydrofluorination. UF_4 samples having UO_2F_2 and UO_2 content higher than 2.5 wt% are not desired for plant scale batches and are rejected. Such samples were collected for our study along with the ones having these constituents below 2.5 wt%. For the sake of simplicity and ease of calculation in thermodynamic analysis, the mixed oxide (or AOI) has been considered as UO_2 and hence referred to as UO_2 thereafter. The starting uranium fluoride was analyzed for UO_2F_2, UO_2, free acidity and moisture content. Selective dissolution of UO_2F_2 from a sample of the green salt was carried out by adding methanol into the green salt, and the solution was filtered. The filtrate was analyzed for optical density of UO_2F_2 using UV–Visible Spectrophotometer and compared with the standard to determine the concentration of UO_2F_2 in the green salt. To analyze mixed oxide content in the green salt, a known quantity of the salt was added to ammonium oxalate solution, whereby UF_4 and UO_2F_2 dissolved in ammonium oxalate, but the oxides remained insoluble. The solution was filtered, and the residue containing ammonium oxalate insoluble (AOI) in the form of mixed oxides, was weighed, then heated to 105 °C (378 K) to remove water and weighed again. The resultant weight was the weight of the mixed oxide and then weight per cent was calculated. Moisture and free acidity were determined by thermogravimetry and volumetric analysis respectively. UO_2F_2 content, mixed oxide (referred as UO_2) content, moisture and free acidity, thus determined for the five samples of UF_4 are reported in Table 1.

The moisture content and free acidity thus determined were found to be below 0.1 wt% for all the UF_4 samples. Hence, their effect is similar in all the batches. Moreover, they get eliminated under vacuum and flowing argon. Hence, their effect has been ignored in further thermodynamic analysis. Evacuation and argon purging is done three times, and every time argon is at a slight positive pressure (770 mmHg) and thereafter continuous argon flow is maintained.

The morphology and particle size distribution of a representative UF_4 sample are presented in Fig. 1(a) and (b) respectively.

Table 1
UO_2F_2, UO_2, moisture and free acidity contents in the different samples of UF_4 used for the studies.

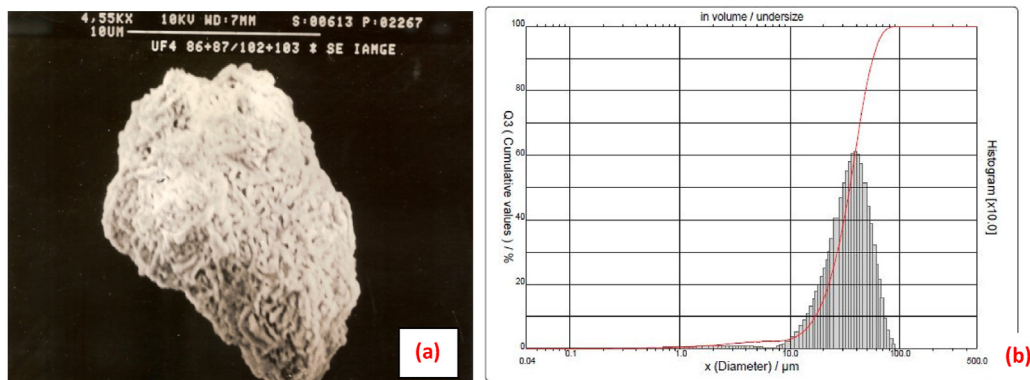| Sr. No.	Wt% UO_2F_2 (x)	Wt% UO_2 (y)	Moisture (wt%)	HF (wt%)
1.	6.67	0.10	<0.1	<0.1
2.	0.99	2.01	<0.1	<0.1
3.	9.23	0.10	<0.1	<0.1
4.	3.15	4.28	<0.1	<0.1
5.	2.40	0.17	<0.1	<0.1

Fig. 1. (a) SEM of UF_4 powder. (b) Particle size distribution of UF_4 (obtained by laser diffraction technique).

Calcium metal used for reduction was in the form of granules of >99.8% purity. The sieve analysis of Ca granules is reported in Table 2.

2.2. Design of the reactor and the experimental setup

Calciothermic reduction of UF_4 was carried out in a resistive pit type furnace. For these small scale experiments of calciothermic reduction of UF_4, a specially designed lining less graphite reactor was used. The dimensions of the reactor and its actual photograph are shown in Fig. 2(a) and (b) respectively. To minimize carbon pick up from the graphite reactor, an impervious coating of yttria was done on the reactor. The slurry coating of yttria was applied as per the procedure described by Banker et al. [18,19]. The carbon pickup was thereby found to reduce to less than 200 ppm.

2.3. Experimental procedure

UF_4 was blended with calcium metal granules in a double cone type blender. For each of the five batches, the charge comprised of 2700 g UF_4 and 1032 g Ca (Ca taken in 50% excess over the stoichiometric requirement, UF_4/Ca ratio ~ 2.6). The blending speed and blending time were optimised at 17 rpm and 30 min respectively, which yielded a homogeneous blended mixture. This mixture was charged in the graphite reactor layer by layer with intermediate tapping (for compacting the charge) and then capped with pre heated CaF_2. The CaF_2 layer was rammed all over the surface to make a dense bed of the capping, with a thickness of about 25 mm (~1 inch). The graphite reactor was then put inside a leak tight inconel 600 retort for heating. The retort housing the reactor was evacuated and purged with argon three times and then continuous argon flow was maintained to ensure inert atmosphere. A schematic of the experimental setup is shown in Fig. 2(c). The charge was then heated in a pre-defined temperature schedule as illustrated in Fig. 3. Initially, the charge was allowed to homogenize for 45 min at 200 °C (473 K) to ensure uniform temperature

distribution in the entire charge volume and avoid the occurrence of any premature reactions. Then, it was heated at 650 °C (923 K), a little above the firing temperature of 500 °C (773 K) and soaked for 2 h at this temperature [14,20]. The reaction occurs spontaneously. In all the five experiments, metal ingot clearly separated from slag was obtained, having a typical recovery of greater than 90%. Fig. 4 shows a typical U ingot obtained in these experiments.

The experimental conditions have been standardized, and kept same for all the batches and the only process variables impacting the recovery in every batch are UO_2F_2 and UO_2 contents in the starting fluoride. Hence, any other parameter affecting the course of the reaction will have similar impact on all the reduction batches and thus may be ignored for the present comparative study.

3. Results & discussion

3.1. Thermodynamic calculations for the final temperature attained by the charge

The calciothermic reduction of UF_4 is an exothermic reaction even if triggered at room temperature. Galkin et al. have reported a theoretical final temperature of the charge as 2100 °C (2373 K) through a thermodynamic calculation during the reduction of UF_4 by Ca when initiated at room temperature; and the actual temperature of the process to be 2000 °C (2273 K) as measured with a thermocouple [21]. The liberated heat is therefore sufficient to melt the products as well as for overheating the products to ensure efficient slag-metal separation under adiabatic condition. Hence, calciothermic process, in contrast to magnesiothermic process, does not need preliminary heating of the charge [21]. However under non adiabatic condition, we need to provide pre-heating up to a certain temperature. This is to ensure that the products are in molten state for required prolonged time to separate out due to density difference. Based on literature and past experience, a pre-heating of 500 °C (773 K) is found to be sufficient to fire the calciothermic reduction reaction of UF_4 to U metal [14,20].

The system can be assumed to be under nearly adiabatic conditions, when the batch size is larger (few hundred kilograms). However, when batch size is smaller (few kilograms), heat losses are prone to occur due to increased surface area to volume ratio. In such a case, a higher UO_2F_2 content in the starting fluoride can be beneficial, since it offers higher heat of reaction with Ca as compared to UF_4. Also, preheating adds an additional heat to the system, i.e. the heat input into the reactants when they are heated from room temperature up to 500 °C (773 K) [14,20]. This total heat is manifested in the system as a rise in temperature of the products much above the melting point of CaF_2, and thus can accommodate

Table 2
Sieve analysis of the calcium granules used for reduction experiments.

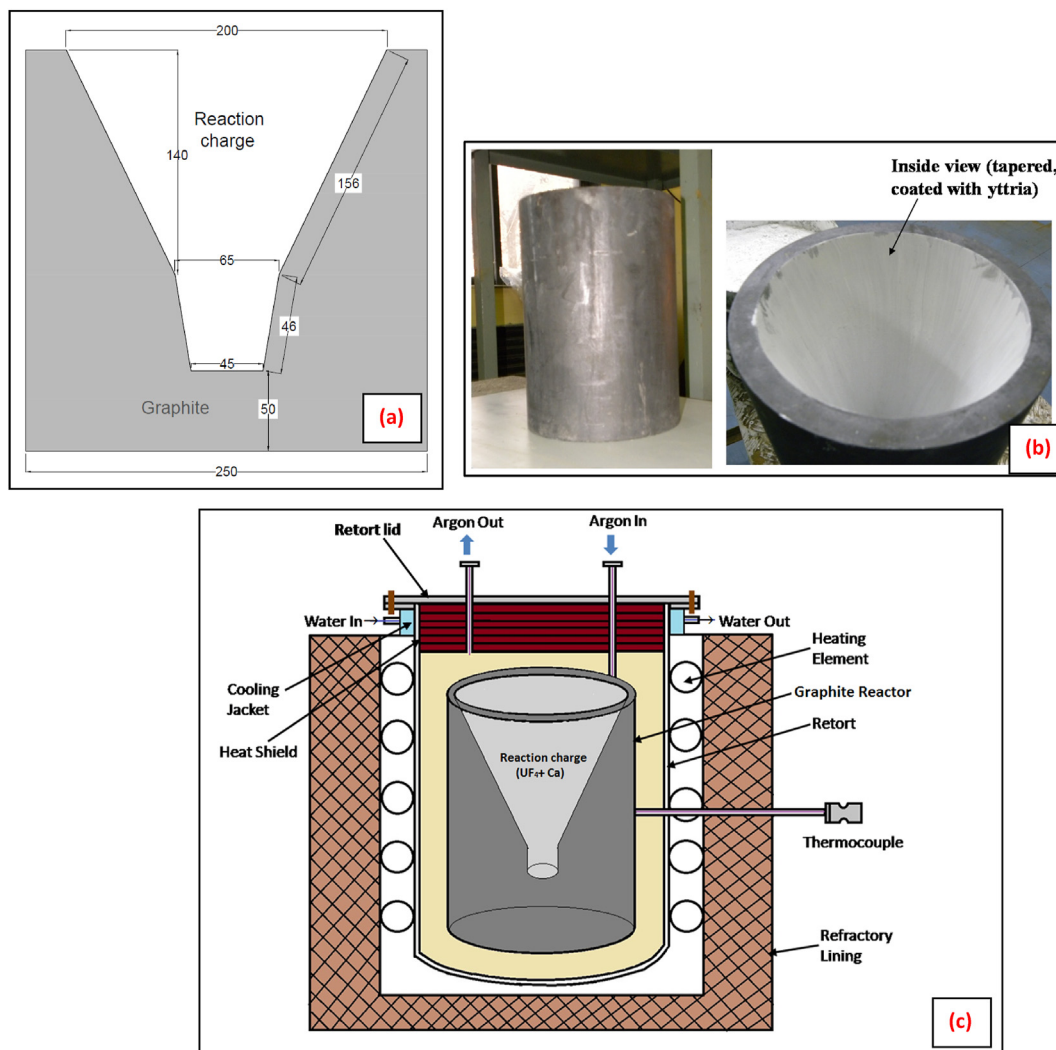| Sr. No.	ASTM Sieve Specification (mm)		% Retention
1.	+10	+2.0	10—12
2.	−10 to +20	−2.0 to +0.84	80 ± 2
3.	−20 to +30	−0.84 to +0.59	7 max
4.	−30 to +40	−0.59 to +0.44	1.5 max
5.	−40 to +50	−0.44 to +0.297	0.3 max
6.	−50 to +60	−0.297 to +0.25	0.1 max
7.	−60	−0.25	0.05 max

Fig. 2. (a) Graphite reactor (schematic), all dimensions are in mm (b) Graphite reactor (actual photograph, with yttria coating inside), (c) The experimental setup for calciothermic reduction experiment.
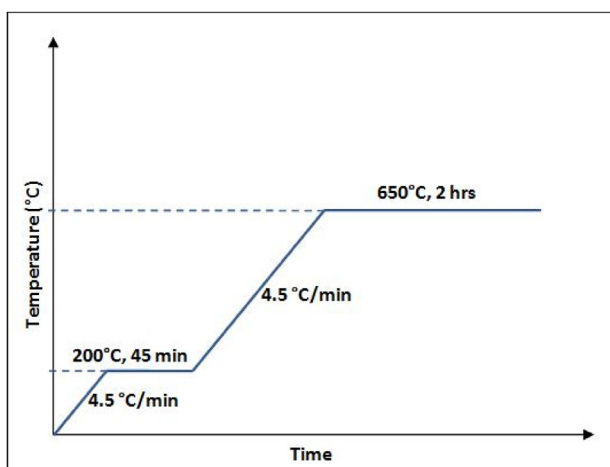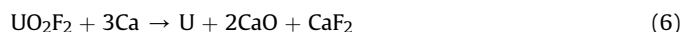

Fig. 3. Temperature-time curve for the heating schedule employed for the calcio-thermic reduction experiments.

the heat losses in the system as well as ensure sufficient superheat above the melting point for the products for complete slag-metal

separation. This study serves to provide a thermodynamic calculation for the final temperature attained by the products.

UF$_4$ usually contains moisture and free acidity in the form of HF, apart from the water soluble content (UO$_2$F$_2$) and ammonium oxalate insoluble (UO$_2$) content in the form of mixed oxides [9,11]. The different reactions that occur in the system are:

$$UF_4 + 2Ca \rightarrow U + 2CaF_2 \tag{5}$$

$$UO_2F_2 + 3Ca \rightarrow U + 2CaO + CaF_2 \tag{6}$$

$$UO_2 + 2Ca \rightarrow U + 2CaO \tag{7}$$

$$Ca + 2HF \rightarrow CaF_2 + H_2 \tag{8}$$

$$CaF_2 + H_2O \rightarrow CaO + 2HF \tag{9}$$

Moisture and free acidity are less than 0.1%, and at higher temperature of the system and under flowing argon, get eliminated. Hence, the effect of the reactions (8) and (9) on the final temperature of the charge can be ignored. The available heats of the exothermic reactions (5) to (7) due to pre-heating at 500 °C (773 K) will cause rise in the temperature of the products U, CaO, CaF$_2$ and
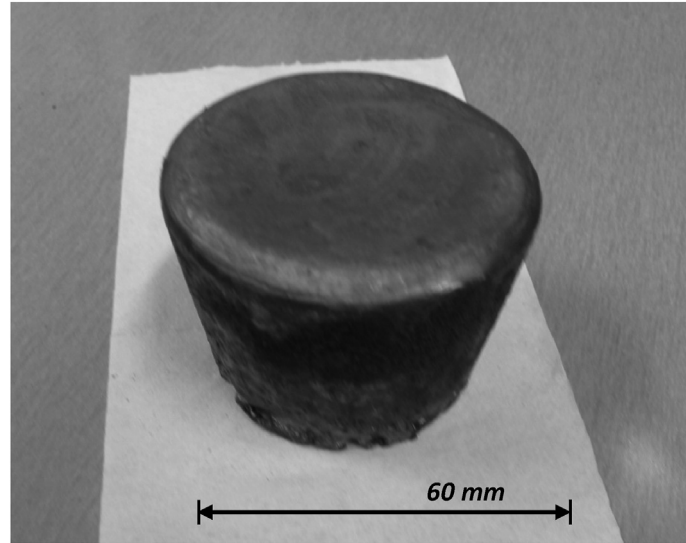
Fig. 4. Typical U metal ingot obtained in calciothermic reduction of UF$_4$ in the present study.

excess calcium. The final temperature T attained by the products can be calculated using the equation:

(Heat of the overall reaction at 773 K) + (Heat input into the reactants by heating from room temperature (i.e. 298K) up to 773 K) = (Heat taken up by the products so that the temperature rises from 773 K to the final temperature T) (10)

The moles of the reactants and products can be calculated (for simplification, calculation is based on 100 g of green salt and 38.2 g Ca, UF$_4$/Ca ratio ~ 2.6 as mentioned in Section 2.3) as shown in Table 3. Molecular weights of UF$_4$, UO$_2$F$_2$, UO$_2$ and Ca are 314.028 u, 308.028 u, 270.028 u and 40 u respectively.

x and y in Table 3 are wt% UO$_2$F$_2$ and wt% UO$_2$ respectively. Equation (10) for the final temperature attained by the products can be represented as:

Table 3
Moles of the reactants and products present in the charge (based on 100 g of green salt).

Name of the Component	Moles present in the charge
UF$_4$	$N_1 = \dfrac{100 - x - y}{314.028}$
UO$_2$F$_2$	$N_2 = \dfrac{x}{308.028}$
UO$_2$	$N_3 = \dfrac{y}{270.028}$
Ca (initially taken)	$N_4 = \dfrac{38.2}{40}$
U	$N_5 = N_1 + N_2 + N_3$
CaF$_2$	$N_6 = 2N_1 + N_2$
CaO	$N_7 = 2N_2 + 2N_3$
Excess (Unreacted) Ca on the product side	$N_8 = N_4 - 2N_1 - 3N_2 - 2N_3$

$$(\Delta H_1 N_1 + \Delta H_2 N_2 + \Delta H_3 N_3) + \left(N_1 \int_{298}^{773} C_p(UF_4)dT + N_2 \int_{298}^{773} C_p(UO_2F_2)dT + N_3 \int_{298}^{773} C_p(UO_2)dT + N_4 \int_{298}^{773} C_p(Ca)dT \right)$$

$$= N_5 \int_{773}^{T} C_p(U)dT + N_6 \int_{773}^{T} C_p(CaF_2)dT + N_7 \int_{773}^{T} C_p(CaO)dT + N_8 \int_{773}^{T} C_p(Ca)dT \qquad (11)$$

where ΔH_1, ΔH_2 and ΔH_3 are heats of the reactions (5), (6) and (7) respectively, representing heats of reaction per mole of UF$_4$, UO$_2$F$_2$ and UO$_2$ respectively, with Ca; and N_1, N_2 and N_3 are moles of UF$_4$, UO$_2$F$_2$ and UO$_2$ present in the charge respectively. The enthalpies of transformation of the different components of the charge, which are required for the calculation of T in equation (11), are listed as under:

$\Delta H_{trans}(U_{(\alpha \to \beta)}) = 2,800\,J/mol,$

$\Delta H_{trans}(U_{(\beta \to \gamma)}) = 4,800\,J/mol,$

$\Delta H_{trans}(U_{(\gamma \to l)}) = 9,200\,J/mol,$

$\Delta H_{trans}(Ca_{(\alpha \to \beta)}) = 930\,J/mol,$

$\Delta H_{trans}(Ca_{(\beta \to l)}) = 8,540\,J/mol.$

Table 4
Data for the calculation of enthalpies of transformation of CaF_2 [23].

Transition at: P, T	dT/dP (deg/kb)	ΔV (cm^3)	ΔS (e.u.)
α–β: 1150 ± 5 °C, 1 atm	−6 ± 1	0.20 ± 0.04	0.8
β–l: 1416 ± 6 °C, 1 atm	10 ± 1	1.76 ± 0.20	4.2

$$\Delta H_{trans}\left(CaF_{2(\alpha \to \beta)}\right) = 4,790.77\ J/mol$$

$$\Delta H_{trans}\left(CaF_{2(\beta \to l)}\right) = 30,023.66\ J/mol$$

The above enthalpies of transformation of U and Ca have been taken from JANAF Thermochemical Tables and [22]. The enthalpies of transformation of CaF_2 have been determined from the following data listed in Table 4, by applying Clausius-Clapeyron Equation [23].

The specific heat of a material is a function of temperature, and the dependence function is different for different allotropes/phases of the material. Table 5 lists the specific heat functions of all the different components of the system of interest in the present study in the different temperature ranges.

The enthalpies of the different reactions occurring in the system at a temperature T can be calculated using the formula:

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_p\ dT \tag{12}$$

where $\Delta C_p = \sum C_{p\ (products)} - \sum C_{p\ (reactants)}$. Using the above relation, the enthalpies calculated for the different reactions at 500 °C (773 K) are reported in Table 6.

Using the given thermodynamic data, the equation for the final temperature (T) attained by the products becomes.

$$(3.54\,x + 4.04\,y)\,T^3 + (2330 - 2.4\,x - 6.99\,y)*10^4\,T^2$$
$$+ (2.71\,y - 2.91\,x - 637)*10^8\,T + (1.44\,x + 1.64\,y)*10^9$$
$$= 0 \tag{13}$$

3.2. Theoretical basis for the maximum tolerable limit of impurities in UF_4

Previous literatures on metallothermic reduction of UF_4 report that the maximum tolerable limit for both the impurities (oxyfluoride and oxide) in the green salt is 2.5 wt% [8,10]. No theoretical

Table 6
Heats of the different reactions occurring in the system at room temperature (298 K) and preheated temperature (773 K).

Reaction	ΔH$_{298}$ (J/mol)	ΔH$_{773}$ (J/mol)
$UF_4 + 2Ca \to U + 2CaF_2$	−539,600	−540,214.83
$UO_2F_2 + 3Ca \to U + 2CaO + CaF_2$	−847,700	−849577.31
$UO_2 + 2Ca \to U + 2CaO$	−184,800	−187,602.65

or experimental basis is available till date for this limit. Kim et al. in their study of the CaO–CaF_2 system, have carried out the experimental determination of the CaO–CaF_2 phase diagram as shown in Fig. 5 [17]. The phase diagram can help to analyze the effect of impurities in UF_4 on the CaF_2 slag which is formed on reduction of UF_4 by Ca. CaO is formed as a result of the reaction of UO_2F_2 and UO_2 with Ca.

Presence of CaO is, in general, thought to increase the overall melting point of the CaF_2 slag due to its very high melting point. However, as can be seen in the phase diagram, presence of CaO initially lowers the melting point of the fluoride slag from 1420 °C to 1362 °C up to 15.30 mol% CaO. The CaO–CaF_2 system is a simple eutectic system with the eutectic reaction $L_{(CaO=15.30\ mol\%)} \to CaO_{(pure\ solid)} + CaF_{2(solid\ solution\ with\ CaO=4.80\ mol\%)}$ occurring at 1362 °C [17]. Thereafter, the melting point again increases, with further increase in the concentration of CaO. However, the melting temperature does not go above the melting point of CaF_2 as long as CaO content is less than or equal to 19 mol% (or 14.40 wt%), i.e. CaF_2 content is 81 mol% (or 85.60 wt%).

CaO content is a combined function of the concentrations of uranium oxyfluoride and oxide. Hence, the maximum tolerable limit of these impurities can be arrived at by using the relation:

$$x_{CaF_2} = \frac{N_6}{N_6 + N_7} \geq 0.81 \tag{14}$$

or

$$\frac{N_6}{N_7} \geq 4.26 \tag{15}$$

, i.e. (moles of CaF_2)/(moles of CaO) ≥ 4.26, which finally reduces to the relation

$$x + 1.23\,y \leq 20.68 \tag{16}$$

which holds true for values of x and y in each of the five cases; where x and y are the weight per cent of UO_2F_2 and UO_2 respectively, as mentioned earlier. Thus, the maximum tolerable limit can

Table 5
Heat Capacities of the different components of the system in the present study [16].

| Element/compound	Specific Heat Capacity, C_p (J/K.mol)	Temperature Range (K)
UF_4	$107.53 + 29.29 \times 10^{-3}\,T - 0.25 \times 10^5\,T^{-2}$	298 < T < 1118
UO_2F_2	$122.93 + 8.62 \times 10^{-3}\,T - 19.87 \times 10^5\,T^{-2}$	T > 298
UO_2	$80.33 + 6.78 \times 10^{-3}\,T - 16.57 \times 10^5\,T^{-2}$	T > 298
Ca	$16.02 + 21.51 \times 10^{-3}\,T + 2.55 \times 10^5\,T^{-2}$	298 < T < 716
	$-0.45 + 41.35 \times 10^{-3}\,T$	716 < T < 1115
	33.47	T > 1115
U	$25.10 + 2.38 \times 10^{-3}\,T + 23.68 \times 10^{-6}\,T^2$	298 < T < 941
	42.93	941 < T < 1049
	38.28	1049 < T < 1408
	48.66	T > 1408
CaF_2	$41.05 + 55.48 \times 10^{-3}\,T + 8.49 \times 10^5\,T^{-2}$	298 < T < 1430
	$154.10 - 729.69 \times 10^5\,T^{-2}$	1430 < T < 1691
	99.16	T > 1691
CaO	$50.42 + 4.18 \times 10^{-3}\,T - 8.49 \times 10^5\,T^{-2}$	298 < T < 2900
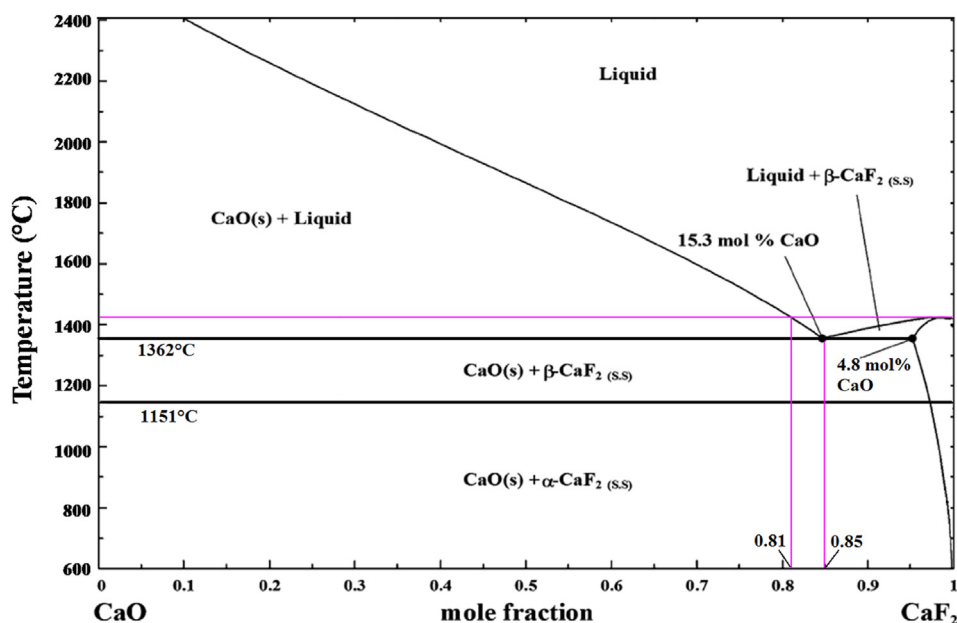
Fig. 5. The CaO—CaF$_2$ phase diagram (© 2012 The Iron and Steel Institute of Japan/ISIJ International. Reproduced with prior permission) [17].

Table 7
Experimental and theoretical observations in different batches of calciothermic reduction of UF$_4$.

Exp. No.	Experimental data			Theoretical data	
	Wt% UO$_2$F$_2$ (x)	Wt% UO$_2$ (y)	Recovery $= \dfrac{Wt.of\ U\ in\ product}{Wt\ of\ U\ in\ input\ material} \times 100$	Tempera-ture (°C)	$x + 1.23\,y$
1.	6.67	0.10	94.50	2554.93	6.79
2.	0.99	2.01	91.50	2465.40	3.46
3.	9.23	0.10	95.00	2591.19	9.35
4.	3.15	4.28	90.60	2485.37	8.41
5.	2.40	0.17	92.98	2494.08	2.61

be much higher than 2.5 wt%, without having any detrimental effect on the reduction characteristics and the recovery, as is clear from Table 7. Instead, higher UO$_2$F$_2$ provides higher heat of reaction leading to a higher final temperature of the charge, enabling better slag-metal separation and increased recovery.

The final recovery (or yield) of uranium in the ingot obtained in the five experiments along with the theoretical final temperature attained by the products, has been reported in Table 7.

From Table 7, it is clear that the final temperature rise in case of expt. 3 (max. UO$_2$F$_2$ content) compared to expt.5 (as per specification) is ~100 °C. The higher temperature is beneficial in small scale reductions. However, in plant scale reduction trials this may not be desirable.

4. Conclusions

1) This study provides a maximum tolerable limit of impurities in the form of a relation between the concentration of oxide and oxyfluoride, which is much higher than 2.5 wt%. Even then, it does not hamper with the final U recovery in the ingot, as the batches which had 6.67 and 9.23 wt% of UO$_2$F$_2$ in the starting fluoride also yielded a final recovery of >90%.
2) The final temperature is higher in case of higher UO$_2$F$_2$ wt%. This increase in temperature, as compared to the temperature obtained with UO$_2$F$_2$ of desired specifications might be difficult to contain for plant scale processes, where the system is already under nearly adiabatic conditions. However, it is useful in

smaller scale (few kilograms) where heat losses are incurred due to smaller size of the system (increased surface area to volume ratio).

5. Conflict of interest disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors **declare** the following financial interests/personal relationships which may be considered as potential competing interests:

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.net.2020.12.021.

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