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Thermal analysis for understanding of mixed oxalate decomposition reaction scheme

Salah AKKACHE¹, Maelig OLLIVIER¹, Eléonore WELCOMME², Loïc FAVERGEON¹

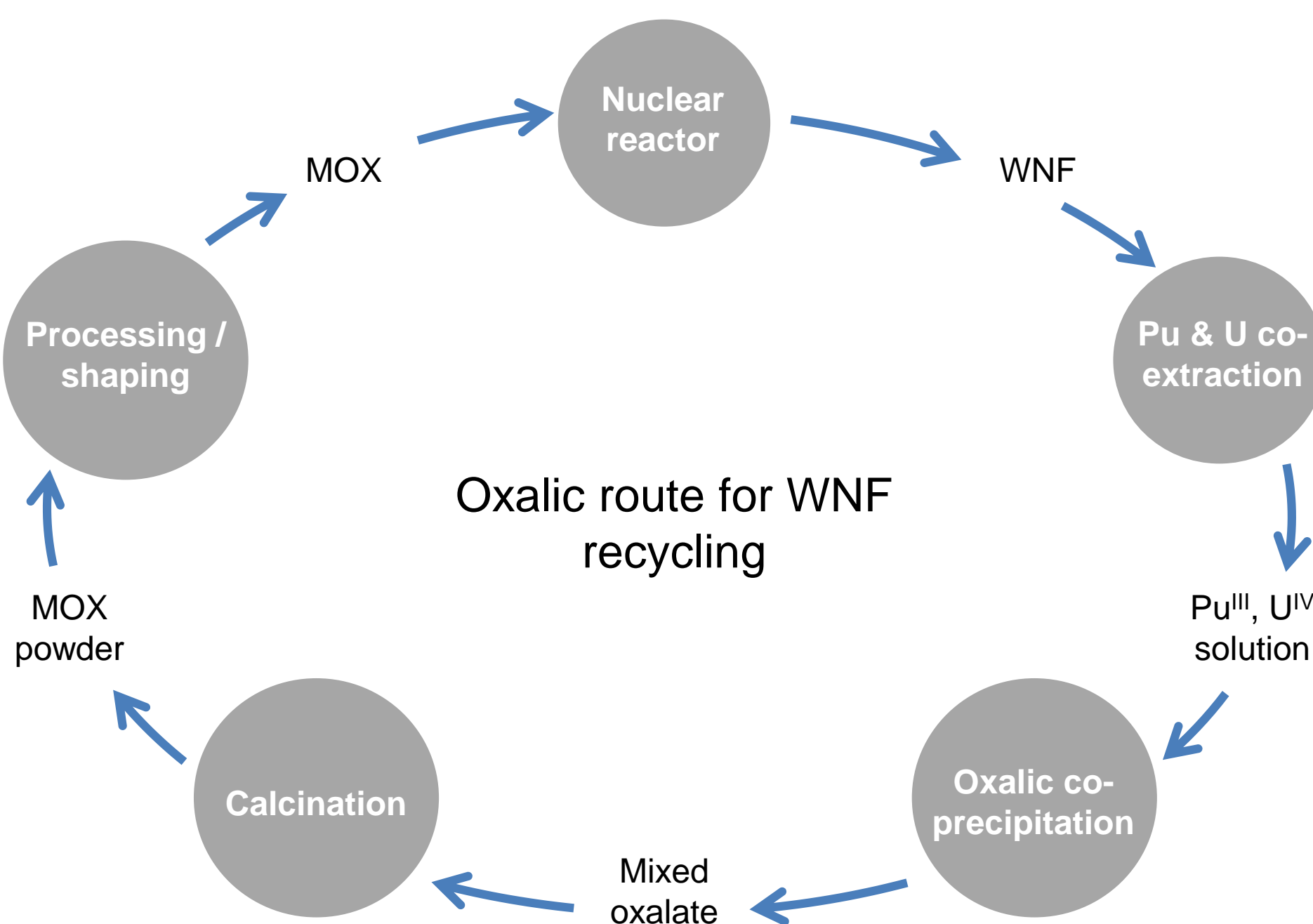
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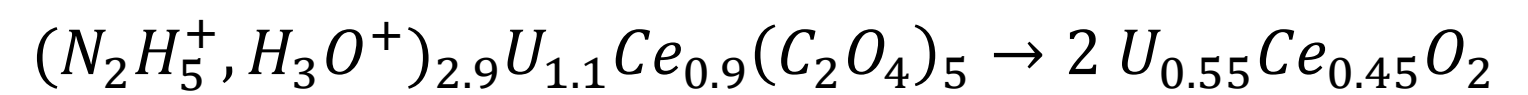
1. Context

- Need of waste nuclear fuel (WNF) recycling
- Need of Plutonium valorization
- Need of WNF recycling efficiency
- Reducing ultimate waste

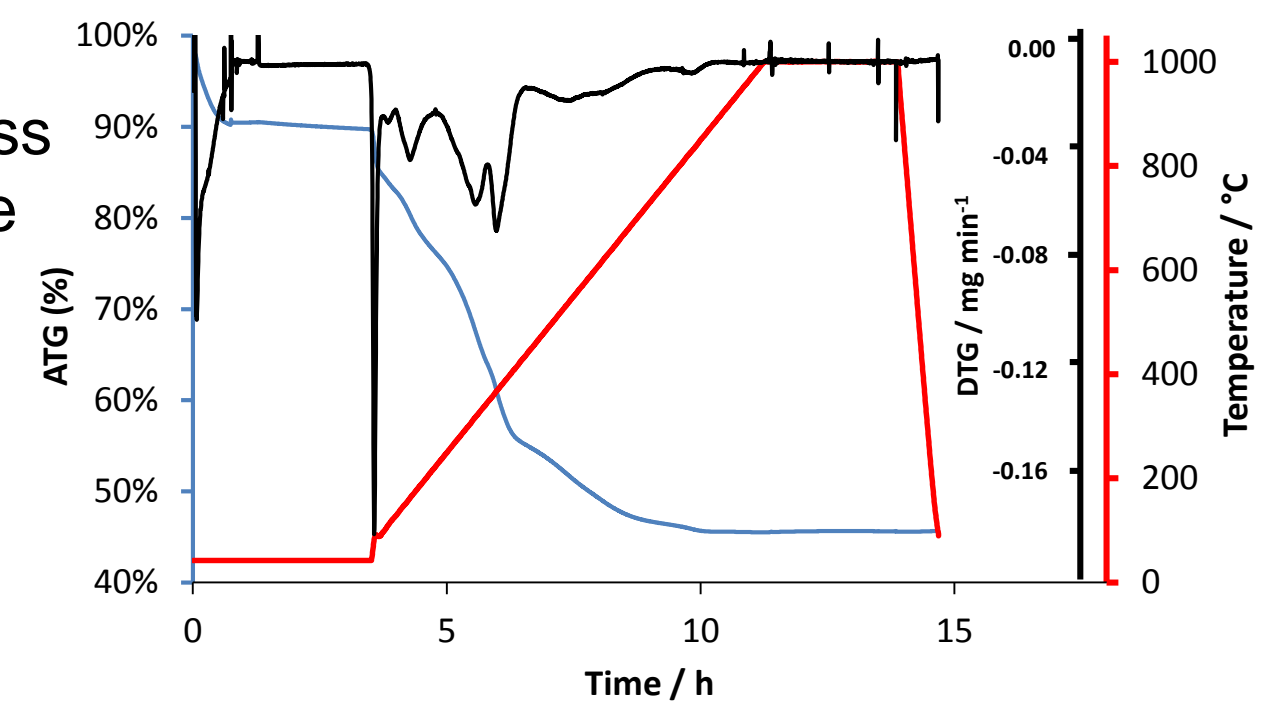
Oxalic way as a potential route for WNF recycling into uranium – plutonium mixed oxide (MOX)



4. Results

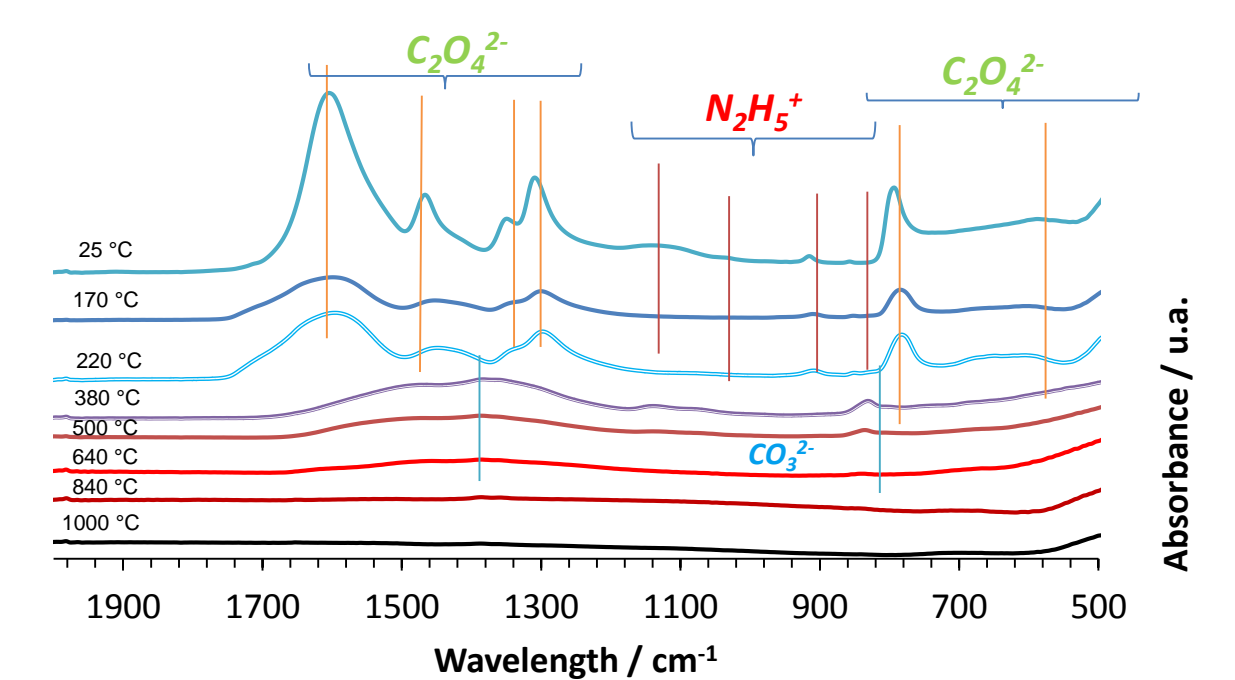


- Six peaks of mass loss
- Reaction temperature identification



- Intermediate synthesis through isothermal experiments
- Target temperatures : 170 °C, 220 °C, 380 °C, 500 °C, 640 °C, 840°C and 1000°C
- Intermediates analysis by Fourier Transform InfraRed (FTIR) [3,4,5]

1. Dehydration at 170°C and 220°C
2. Desperation of oxalate and hydrazinium ions, carbonates ion apparition at 380°C
3. Intensity decrease of carbonate ion peaks then desperation, at 640°C and 840 °C respectively



2. Questions

- The calcination is a key step in MOX production
- The mixed oxalate calcination occurs through title known reaction scheme [1,2].

How the thermal analysis can be used to improve the knowledge about the mixed oxalate decomposition reaction scheme?

3. Experimental approach



Temperature ramp
Reaction scheme
identification

Use of Ce as simulant of Pu
Intermediate analysis

- Gas : mass spectrometry
- Solid : infrared, specific area, SEM

Isotherms
Intermediate analysis /
kinetic modeling

Symmetrical thermo gravimetric analyser TAG Setaram ®

5. Conclusions

- Thermal analysis coupled to intermediates composition analysis allows reaction scheme identification.
- The decomposition of mixed oxalate into MOX involves
 - two dehydration steps
 - Partial decomposition of oxalate and hydrazinium cation
 - The formation of an oxy-carbonate
 - The final conversion into MOX

Temperature / °C	Solid product
20 – 145	$(N_2H_5, H_3O)_{2.9} [U_{1.1}Ce_{0.9}(C_2O_4)_5] \cdot nH_2O$
145– 220	$(N_2H_5, H_3O)_{2.9} [U_{1.1}Ce_{0.9}(C_2O_4)_5]$
220 – 450	$(N_2H_5, H_3O)_{0.9} [U_{1.1}Ce_{0.9}(C_2O_4)_4] + U_{1.1}Pu_{0.9}O_2 (CO_3)_{1.55}$
450 – 850	$U_{1.1}Ce_{0.9}O_2 (CO_3)_{1.55}$
850 - 1000	$2 U_{0.55}Ce_{0.45}O_2$

References

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- [2] A. VENTURIN (2015)
- [3] Nakamoto 2008; DOI:10.1002/9780470405888
- [4] Heintz J. Mater. Sci. 21 (1986) 1569–1573
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