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Thermal analysis for understanding of mixed oxalate decomposition reaction scheme

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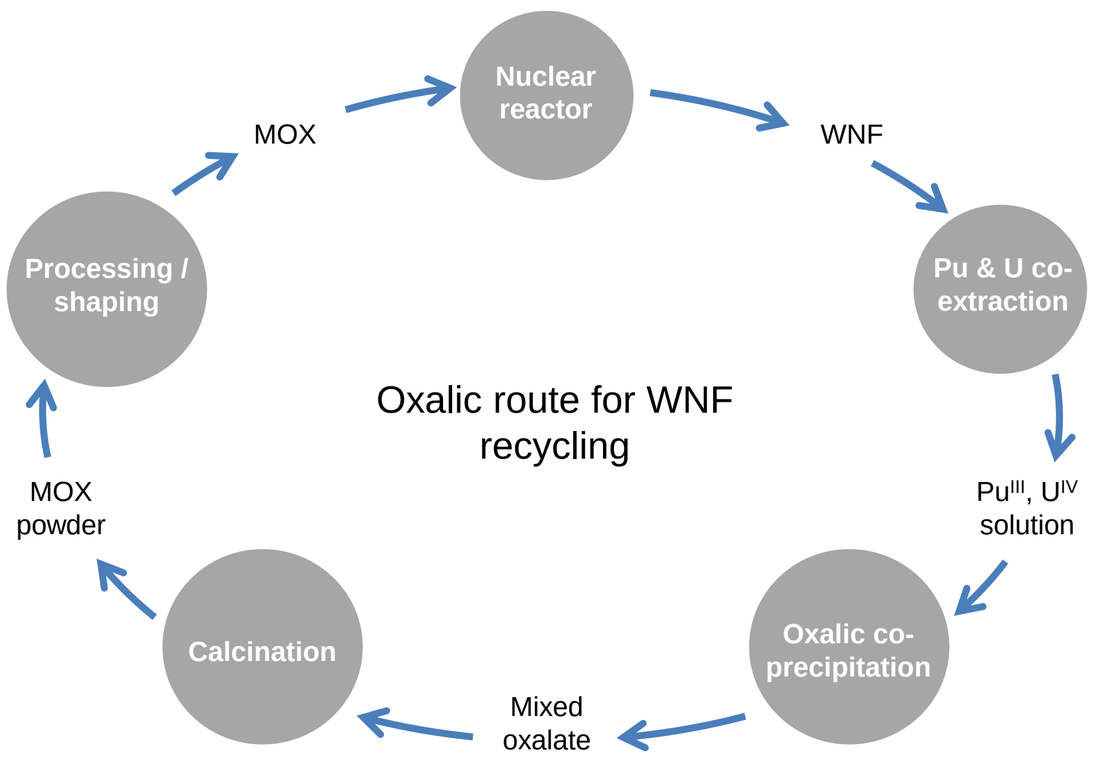
1. Context

- 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)



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

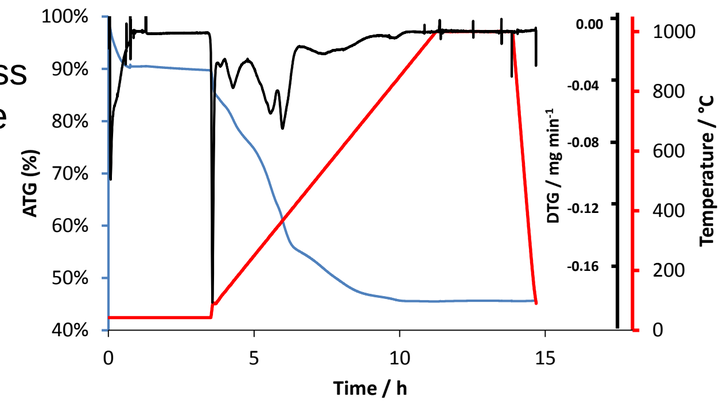
Isotherms
Intermediate analysis / kinetic modeling

Symmetrical thermo gravimetric analyser TAG Setaram ®

4. Results

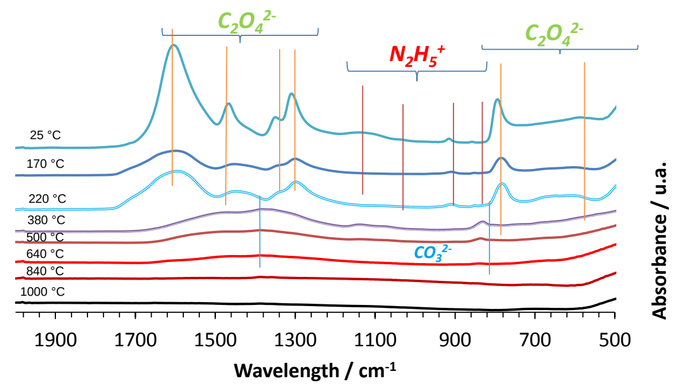
$$(N_2H_5^+, H_3O^+)_{2.9}U_{1.1}Ce_{0.9}(C_2O_4)_5 \rightarrow 2\ U_{0.55}Ce_{0.45}O_2$$

- Six peaks of mass loss
- Reaction temperature identification



- Intermediate synthesis trough isothermal experiments
- Target temperatures : 170 °C, 220 °C, 380 °C, 500 °C, 640 °C, 840°C and 1000°C
- Intermediates analysis by Fourrier 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

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	$(N_2H_5,H_3O)_{\mathbf{0.9}}\,[U_{1.1}Ce_{0.9}(C_2O_4)_{\mathbf{4}}]\ +\ U_{1.1}Pu_{0.9}O_2\,(CO_3)_{\mathbf{1.55}}$
450 – 850	$U_{1.1}Ce_{0.9}O_2\,(CO_3)_{\mathbf{1.55}}$
850 - 1000	$2\ U_{0.55}Ce_{0.45}O_2$

References

[1] L. DE ALMEIDA (2012)
[2] A. VENTURIN (2015)
[3] Nakamoto 2008; DOI:10.1002/9780470405888
[4] Heintz J. Mater. Sci. 21 (1986) 1569–1573
[5] Spectrochim. Acta Part Mol. Spectrosc. 34 (1978) 263–2675

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