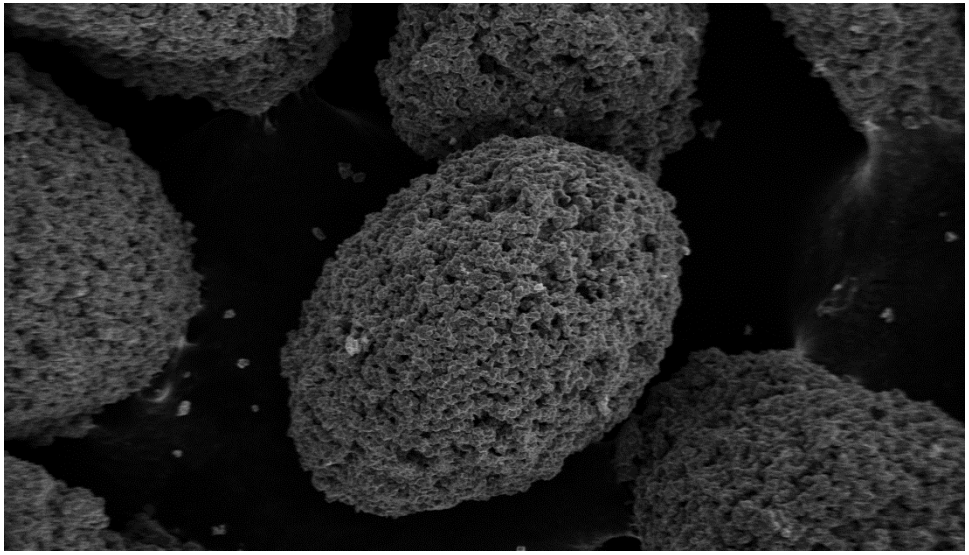
Kinetic Analysis of a $CuFeAlO_4$ oxygen carrier during reduction with H_2 and CO for Chemical Looping combustion applications



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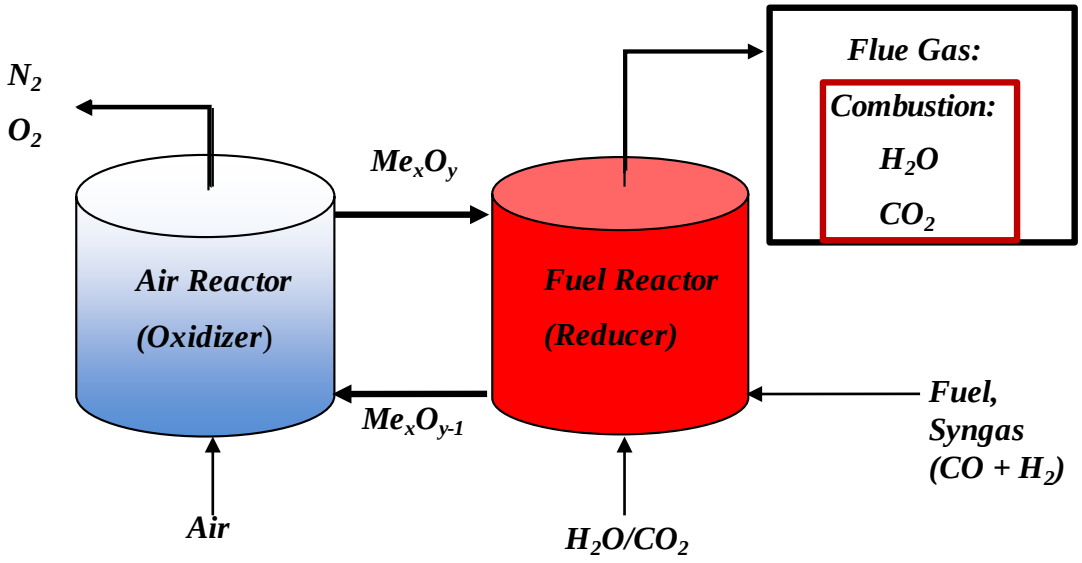
Overview:

- **Background**
  - **Chemical Looping Combustion**
  - **Problem Statement**
- **$CuFeAlO_4$ – Gas Phase System (H_2 and CO)**
  - **Modeling of Gas-Solid Reactions (Underlying assumptions of the SCM model)**
  - **Thermogravimetric Analysis**
  - **Reduction Pathway (Solid State Chemical Changes associated with O^{2-} extraction)**
  - **Physical properties (BCs & Const.)**
  - **Surface Morphology Changes due to reduction (SEM)**
- **Kinetic Modeling**
  - Iso-conversional Techniques (Determination of Conversion dependent activation energy)
  - Model descriptions and comparisons between gas phase components
- **Summary**

Chemical Looping Combustion

- **Configuration:**
  - Dual reactor design:
    - Fuel Reactor (Reducer)
    - Air Reactor (Oxidizer)
- **Foundation:**
  - **Oxygen Carriers**
- **Advantages:**
  - No direct contact between fuel and air.
  - Product stream not diluted with Nitrogen
  - No need for pure oxygen via cryogenic separation



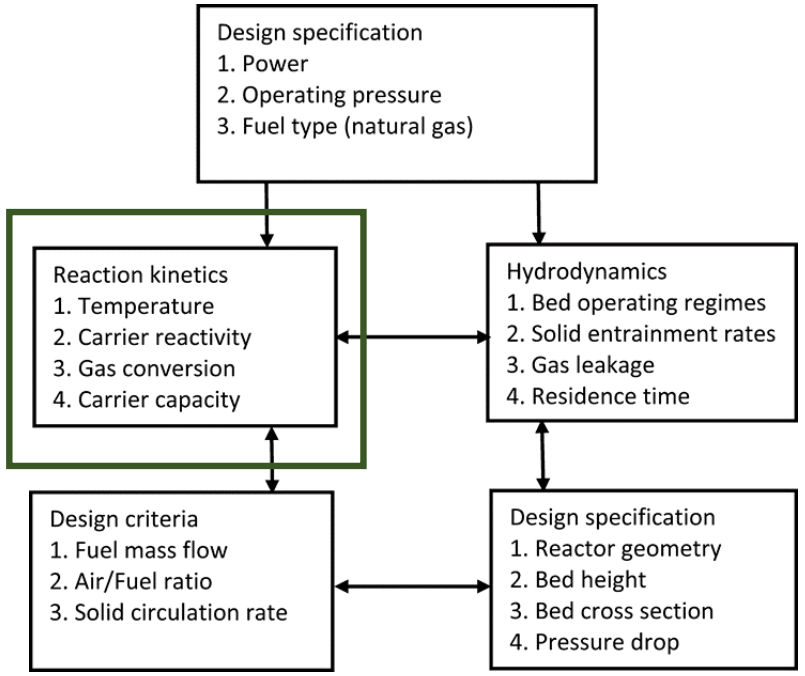
Reduction: Combustion	$(2n+m)Me_xO_y + C_nH_{2m} \rightarrow (2n+m)Me_xO_{y-1} + nCO_2 + mH_2O$	(1)
Syn-Comb H_2	$Me_xO_y + H_2 \rightarrow Me_xO_{y-1} + H_2O$	(2)
Syn-Comb CO	$Me_xO_y + CO \rightarrow Me_xO_{y-1} + CO_2$	(3)
OC Regeneration: **Oxidation**	$Me_xO_{y-1} + (0.5)O_2 \rightarrow Me_xO_y$	(4)

Figure adapted from: [1] Bayham, S., Straub, D., and Weber, J., "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," NETL-PUB-20912; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2016; p 52

Problem Statement and Focus Areas

Motivation:

- ***Reaction Kinetics are a major pillar of CL system design procedures***
- ***Lack of uniformly descriptive models in the literature to explain phenomenological behavior***
- ***Need for descriptive material specific particle scale models for advancement of the CL process concepts***



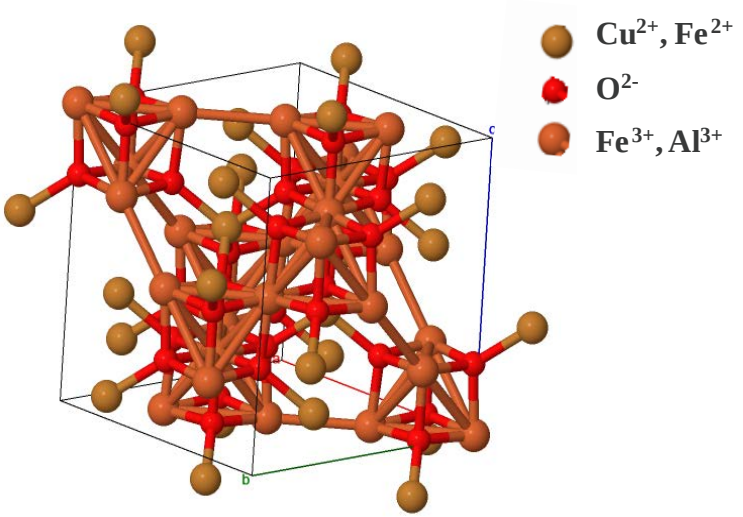
Design procedure for a CL reactor system, adapted from [2]

Focus Area:

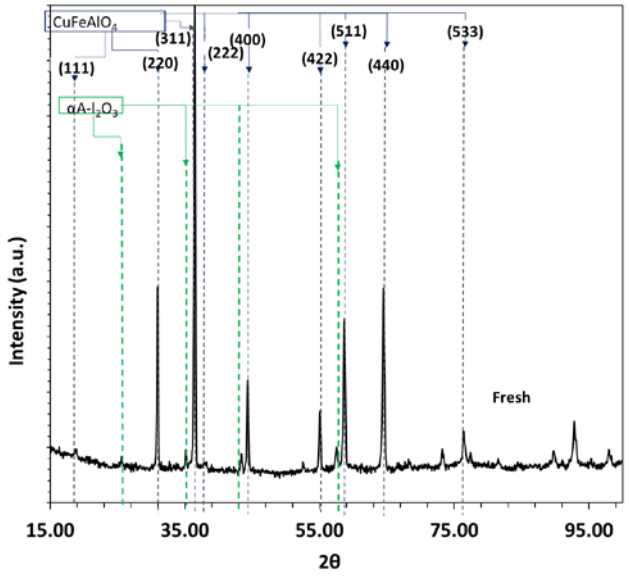
- ***A kinetic analysis of the reduction (with H_2, and CO) for gas phase fueled chemical looping combustion applications to derive particle scale representative models for a $Cu(Fe_{2-x}Al_x)O_4$ oxygen carrier.***
- ***$CuFeAlO_4$***

[2] J. Li, H. Zhang, Z. Gao, J. Fu, W. Ao and J. Dai, "CO2 Capture with Chemical Looping Combustion of Gaseous Fuels: An Overview," Energy and Fuels, vol. 31, pp. 3475-3524, 2017.

$CuFeAlO_4$ – Gas Phase System



Crystal Structure of $Cu(Fe_{2-x}Al_x)O_4$ $(0 \leq x \leq 2)$ spinel in cubic phase



Synthetic OC currently in development for pilot scale applications

Key Modeling Questions:

(1) How does the oxygen carrier change with extent of solid conversion?

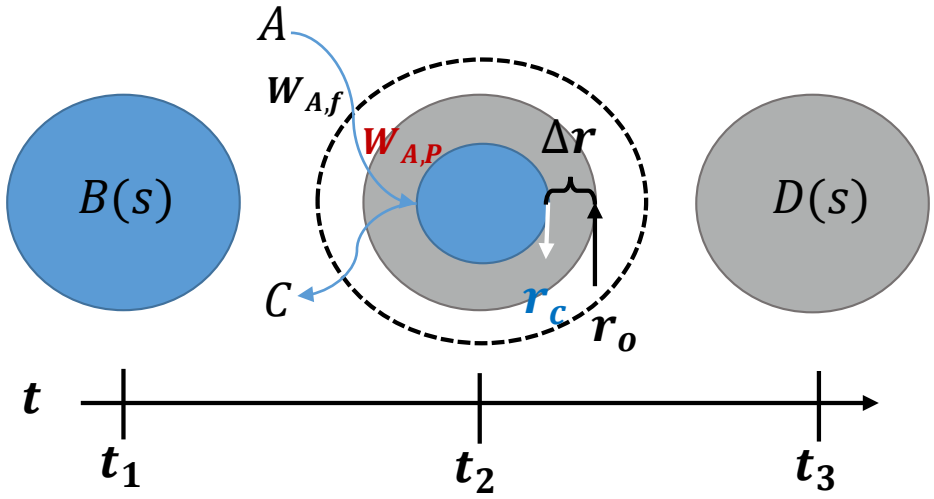
- **Chemical Properties:**
  - **Phase, *Lattice alterations***
- **Physical Properties**
  - **Particle Size**
  - **Surface Area/Porosity**
  - **Skeletal and Bulk Density**

(2) What types of interfaces exist for oxygen transfer and what is their impact on the transfer rate?

Conceptual model for Gas-Solid Reaction Systems:

Shrinking Unreacted Core Model

$$aA(g) + bB(s) \rightarrow cC(g) + dD(s)$$



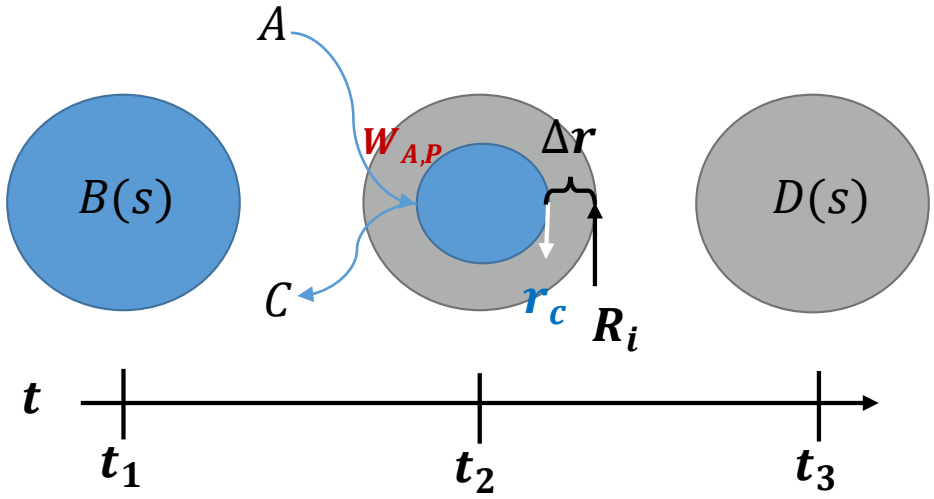
- $\frac{\partial C_i}{\partial t} + \nabla N_i = \bar{R}_i$, ***Continuity Eq.***
  - $C_i = conc.of\ ith\ component$
  - $N_i = molar\ flux\ of\ ith component$
  - $\bar{R}_i = molar\ rate\ of\ production\ per\ unit\ vol\ ith comp$
- $\frac{\partial C_i}{\partial t} = 0,\ P.S.S.A$

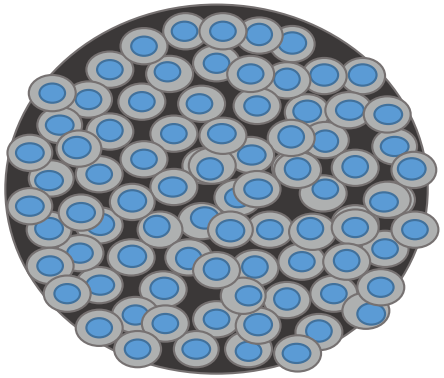
- $r_o > r > r_c, \quad \frac{d}{dr} \cdot \left(r^2 \cdot \frac{dC_A}{dr}\right) = 0$
- BC
  - $\mathcal{D}_e \left(\frac{dC_A}{dr}\right)_{r_c} = k^{"}\ C_{Ac}$
  - $\mathcal{D}_e \left(\frac{dC_A}{dr}\right) = k_g \cdot (C_{Ab} - C_{As})$
- $\frac{\rho_B}{b}\left(\frac{dr_c}{dt}\right) = k^{"}\ C_{Ac},\ r_c|_{t=0} = r_o$
- $X_p = 1 - \left(\frac{r_c}{r_o}\right)^3$
- $$\frac{dX_p}{dt} = \frac{b\frac{3}{r_o} C_A/\rho_B}{\underbrace{\frac{1}{\gamma^2 k_g}}_{film} + \underbrace{\frac{(r_o)}{\mathcal{D}_e}\left(\frac{1}{(1-X_p)^{\frac{1}{3}}} - 1\right)}_{Product\ Layer\ Diffusion} + \underbrace{\frac{1}{(1-X_p)^{2/3}}\frac{1}{k^{"}}}_{reaction}}$$

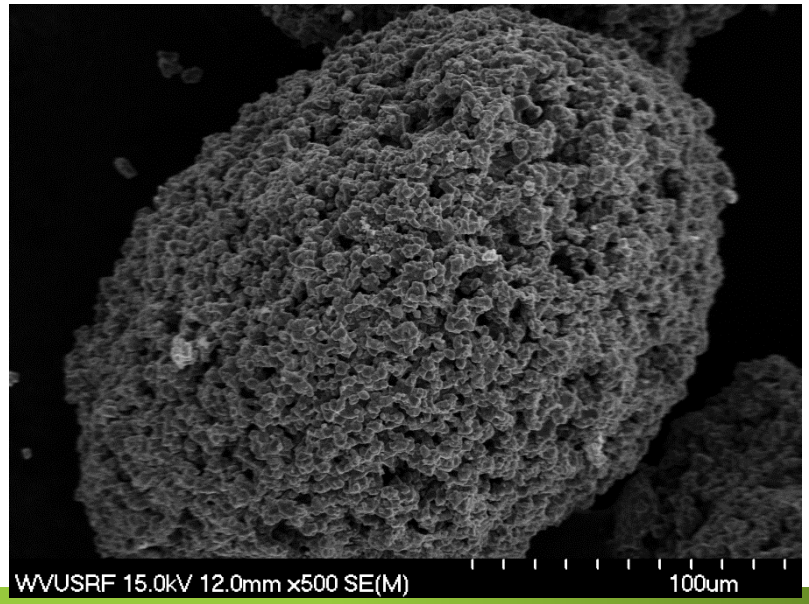
Conceptual model for Gas-Solid Reaction Systems:

Simplified Grainy Pellet Model

$$aA(g) + bB(s) \rightarrow cC(g) + dD(s)$$



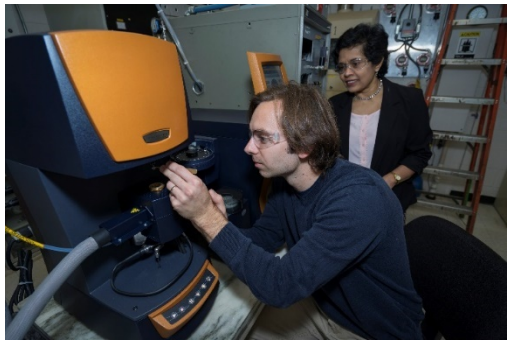




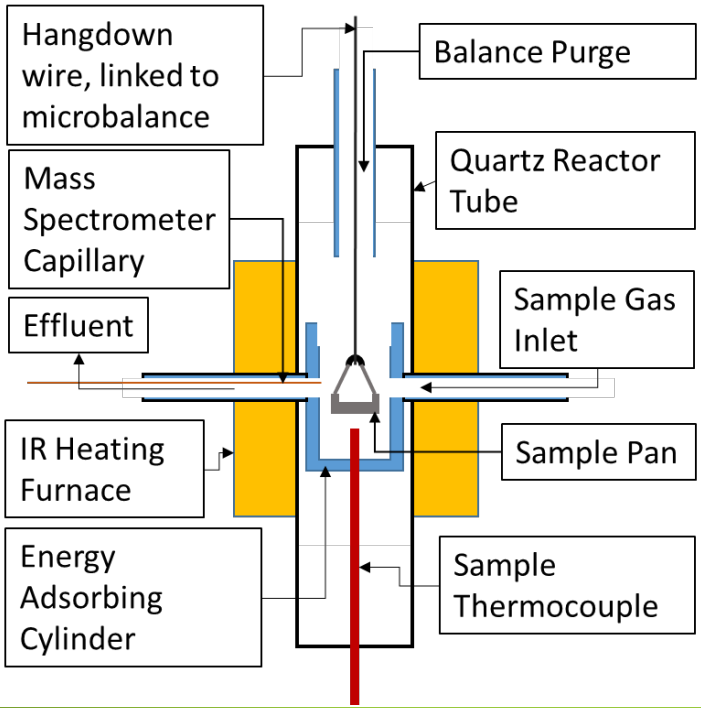
Fundamental Assumptions:

- *The Oxygen carrier grains are considered non porous (≤1m^2/g)*
- *Considered spherical**
- *Size is constant during reaction*
- *Reaction is carried out isothermally*
- *Pseudo-steady state approximation is applicable*

Thermogravimetric Analysis (TGA) of CLC reactions



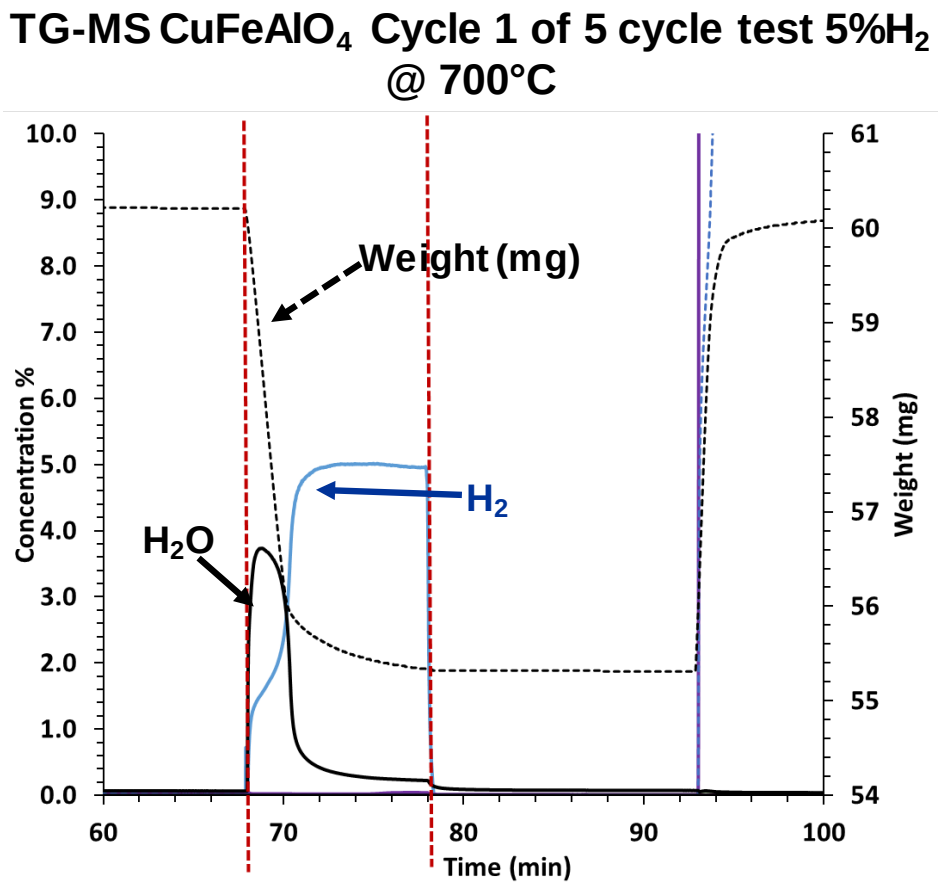
TA Discovery TGA-MS Reactor Setup



TGA-MS

- **Experimental Parameters:**
  - Isothermal Reaction studies
  - Temperature Ranges: 700-850°C, 50°C increments
  - Reducing gas conc: 5-20%H_2 or CO
  - Reduction Time: 10-60 min
  - Oxidizing gas: Air
  - Oxidation Time: 20 min
  - 5 cycles
- **On-line MS for Gas product analysis**
- ***Purpose: Build broad operational scale data matrix for model fitting and validation***

TGA-MS & use for Kinetic Modeling of OCs in CLC



Conventionally:

Extent of conversion: (Overall conversion, TGA)

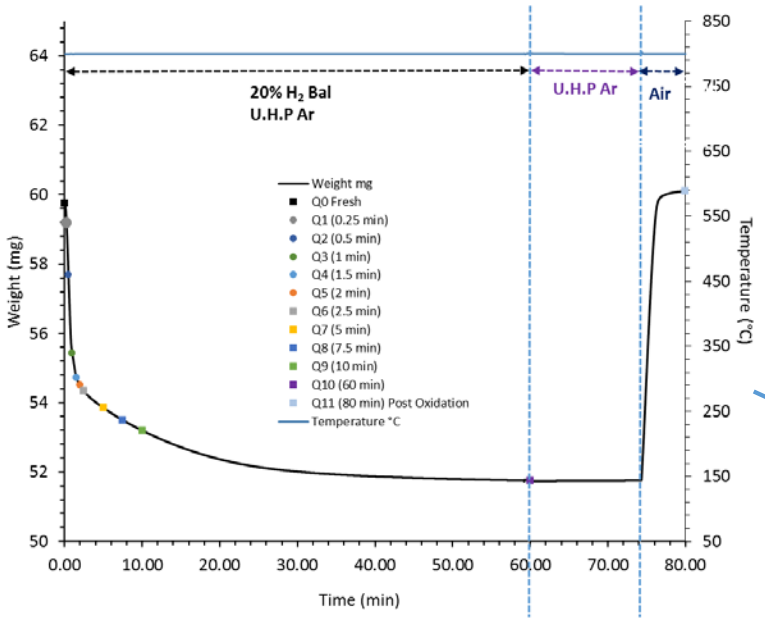
Solid conversion based on instantaneous weight change data

$$X_p(t) = \frac{m_0 - m(t)}{m_0 - m_f}:$$

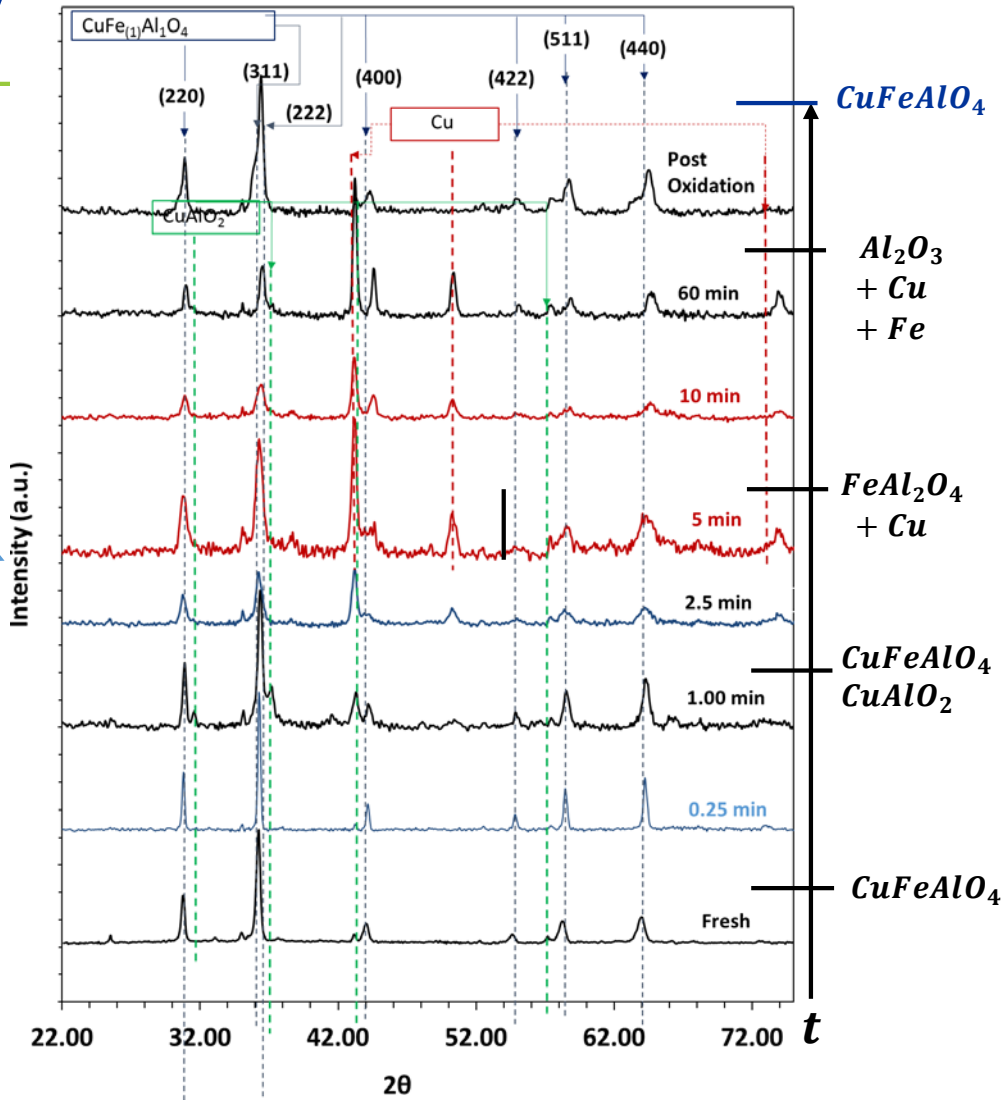
- m_0 = initial mass ($CuFeAlO_4$) (mg)
- $m(t)$ = instantaneous mass at time, t
- m_f = final mass (oxygen depleted Copper-Ferri-Aluminate)

Determining the reduction pathway of $CuFeAlO_4$ Oxygen Carrier

XRD Analysis of TGA Samplings



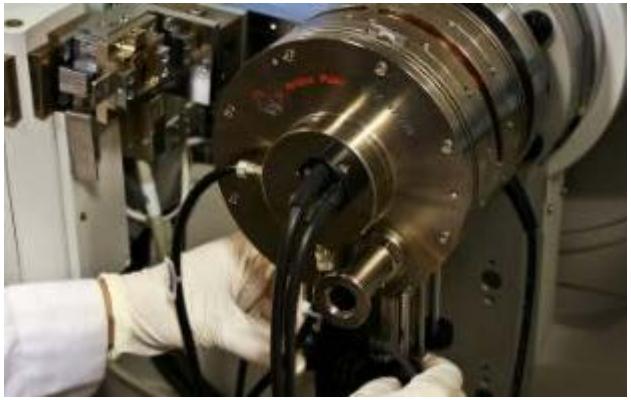
- Phase changes due to reducing gas exposure
  - Possible contributing reduction routes:
  - $Cu(FeAl)O_4 \rightarrow Cu + Fe + 3.5O^{2-} + 0.5Al_2O_3$
  - Intermediates: $FeAl_2O_4$, $CuAlO_2$
  - Theoretical Oxygen Transfer Capacity:14.5%



Reduction pathway-XRD scans of Fresh $Cu(FeAl)O_4$ Oxygen carrier and from controlled reduction during 20% H_2 exposure at 800°C (XRD scans conducted at ambient temperature)

Determining the reduction pathway o $CuFeAlO_4$ Oxygen Carrier

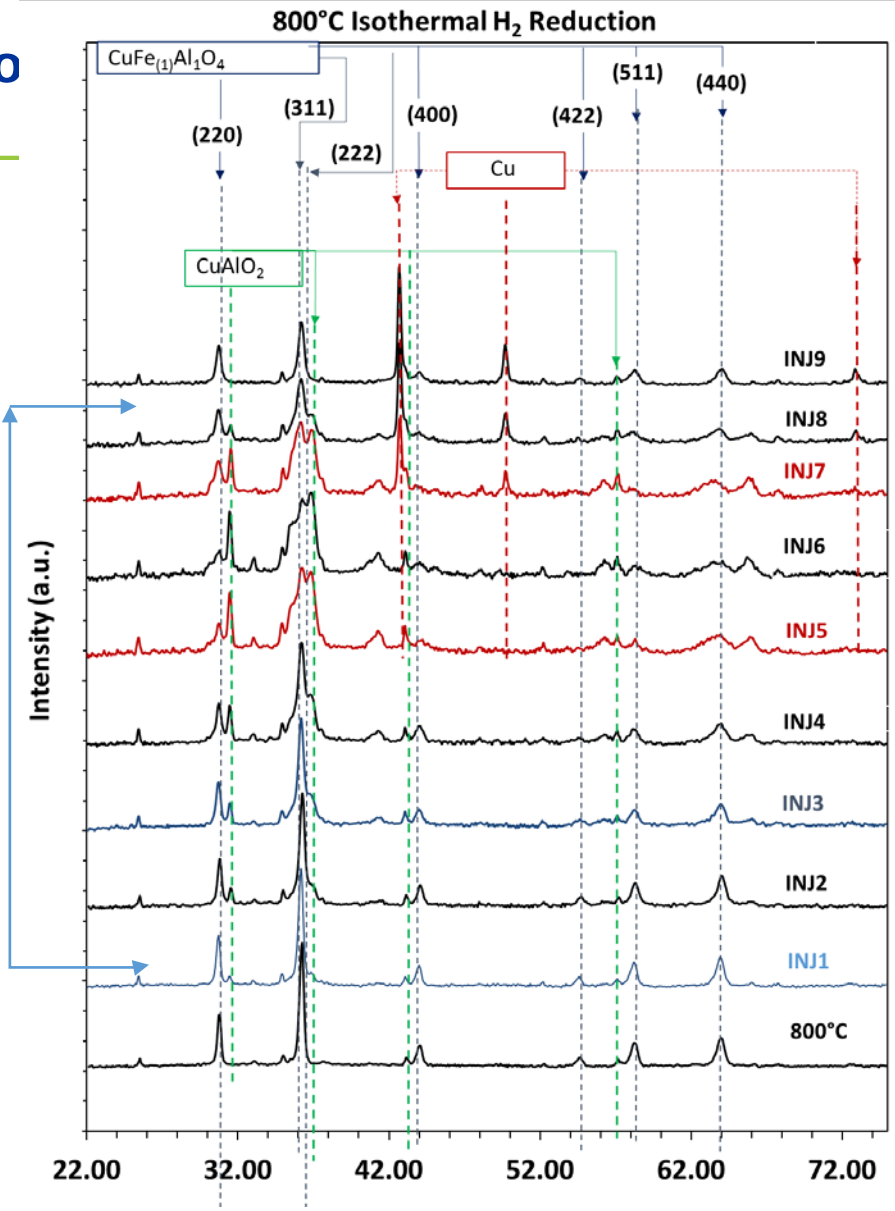
In-Situ High Temperature XRD Analysis



Anton Parr HTK 1200N

- Isothermal: 800°C with Incremental Reduction gas dosing
- Lattice Expansion and Contraction occur simultaneously as $CuFeAlO_4$ spinel is reduced:
  - Formation of $CuAlO_2$ (contraction) and Cu & Al-deficient Fe-Aluminate (expansion)
- Lattice alterations: a=b=c=+0.101 Angstrom followed by -0.130 Angstrom
- Occurs quickly, within the first 1-1.5 min of reduction: (based on ex-situ experiments)
- Final reduced phases confirmed at operating temperature

Within 1.5 minutes of reduction, $X_p = 0.6$

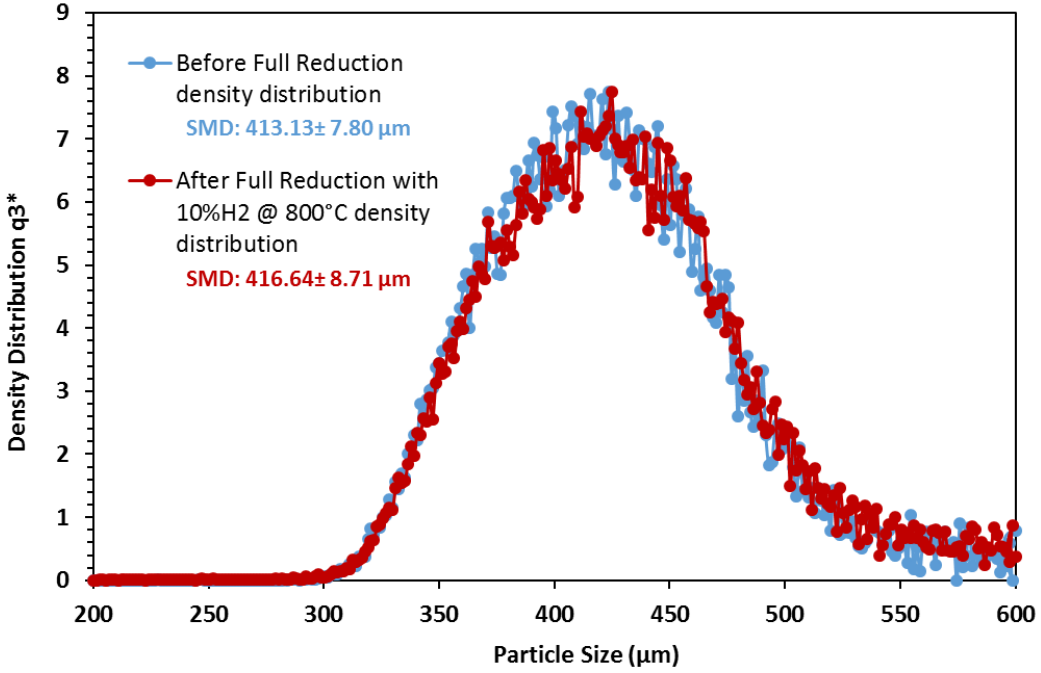


Reduction pathway-In Situ XRD scans of $Cu(FeAl)O_4$ Oxygen carrier with incremental controlled reduction dosing of H_2 at 800°C (XRD scans conducted at 800°C)

Picture from: http://www.uam.es/ss/Satellite/en/1242668321033/1242691900286/UAM_Equipo_FA/equipo/Panalytical_X_Pert__PRO_Theta_Theta_Diffractometer.htm

Extent of Reduction effects on Particle Size Distribution

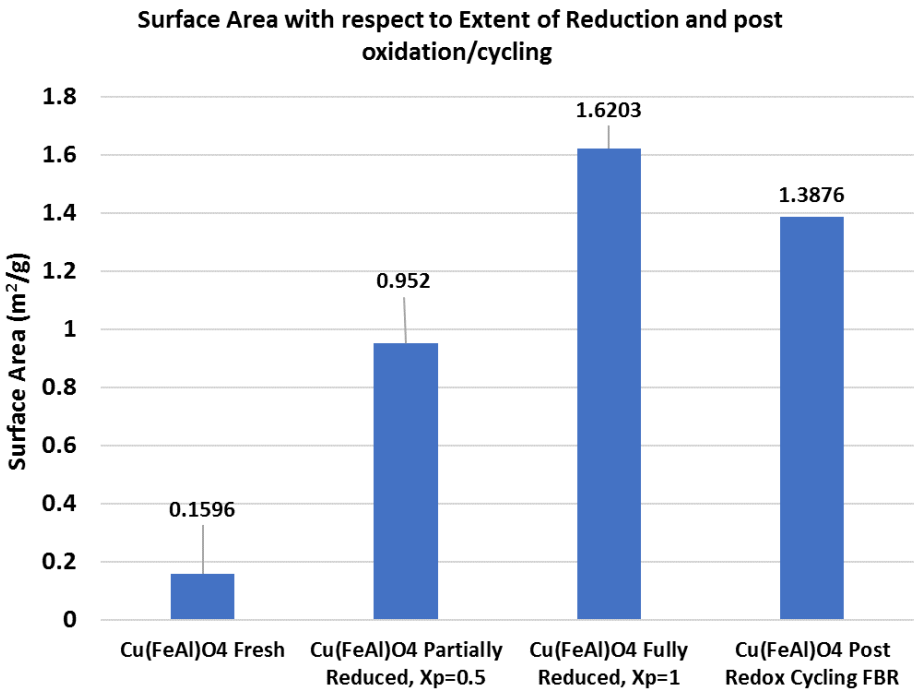
Pellet Size distribution density for Fresh and Fully Reduced OC

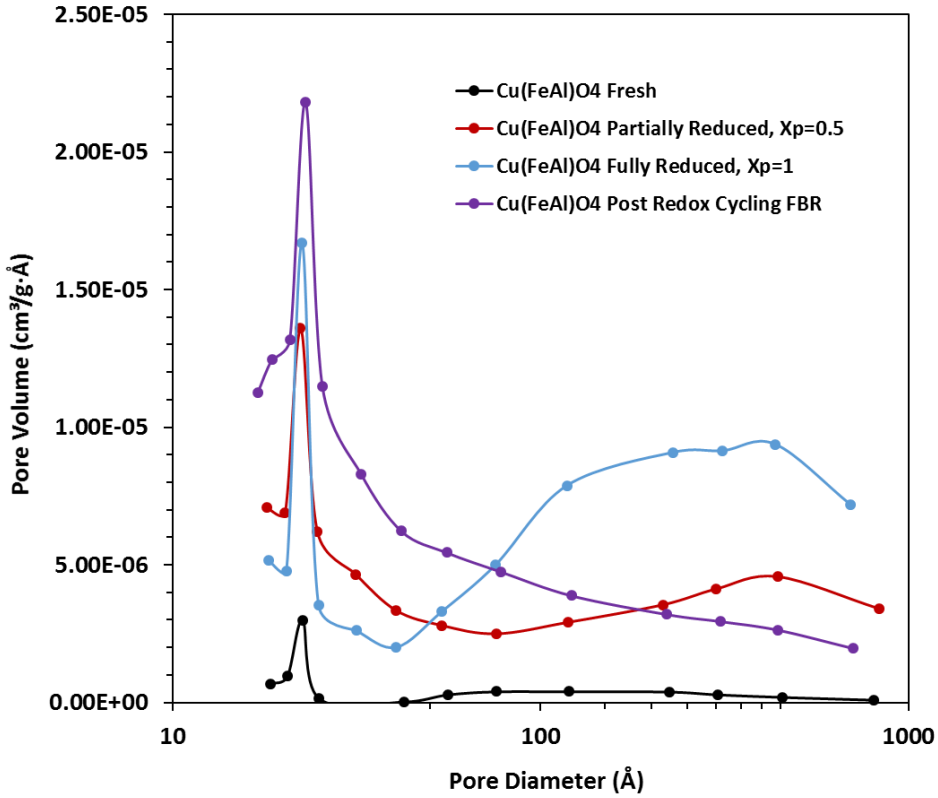


- **Slight shift in Sauter Mean Diameter (SMD). Suggests that there is minimal change in particle size when the material is fully reduced**
- **Macroscopic indicator that grain swelling/shrinkage is not occurring.**

Extent of Reduction effects on Surface Area

Surface Area and Porosity: Micromeritics ASAP 2920

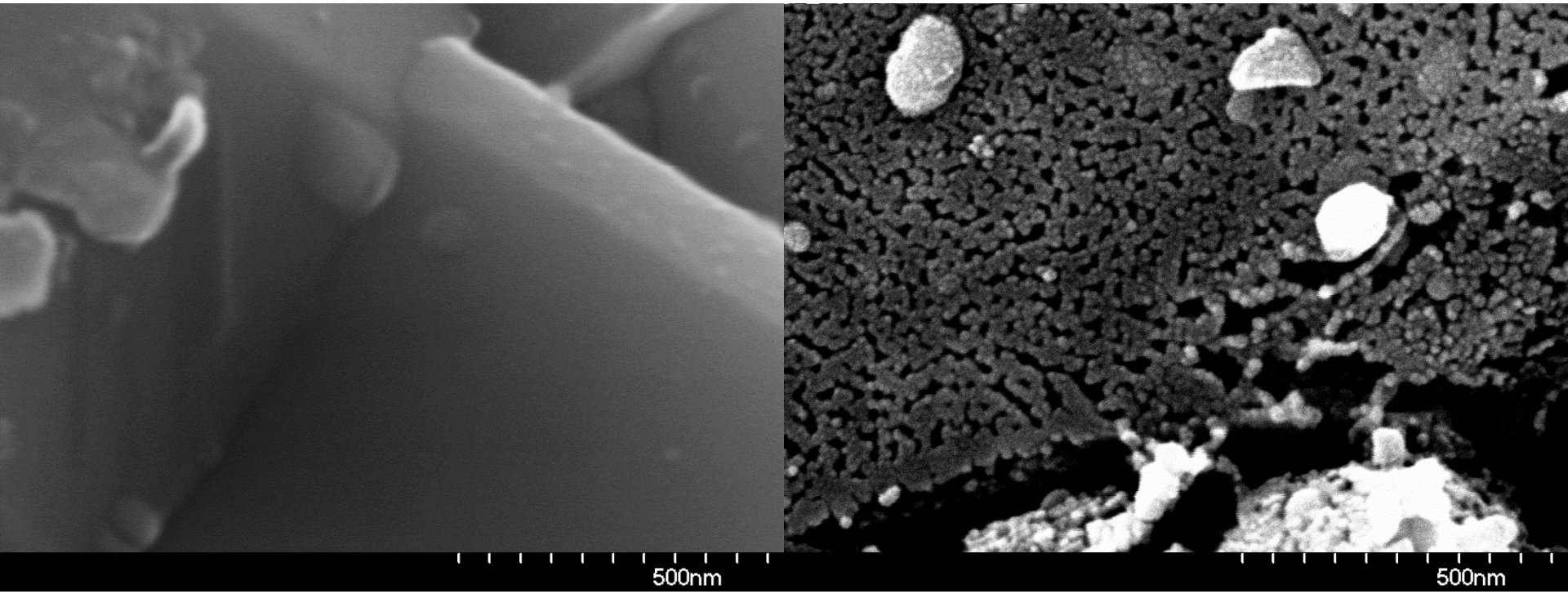




- **Pellet surface area increases with extent of solid conversion**
- **Complementary increase in pore volume associated with ~22Å and 50-800Å pores**
- ***Surface area and micro-porosity maintained after regeneration***

Determining the morphology and surface changes through examination of TGA controlled reduction sampling

SEM Comparative Analysis of Fresh and Partially Reduced OC

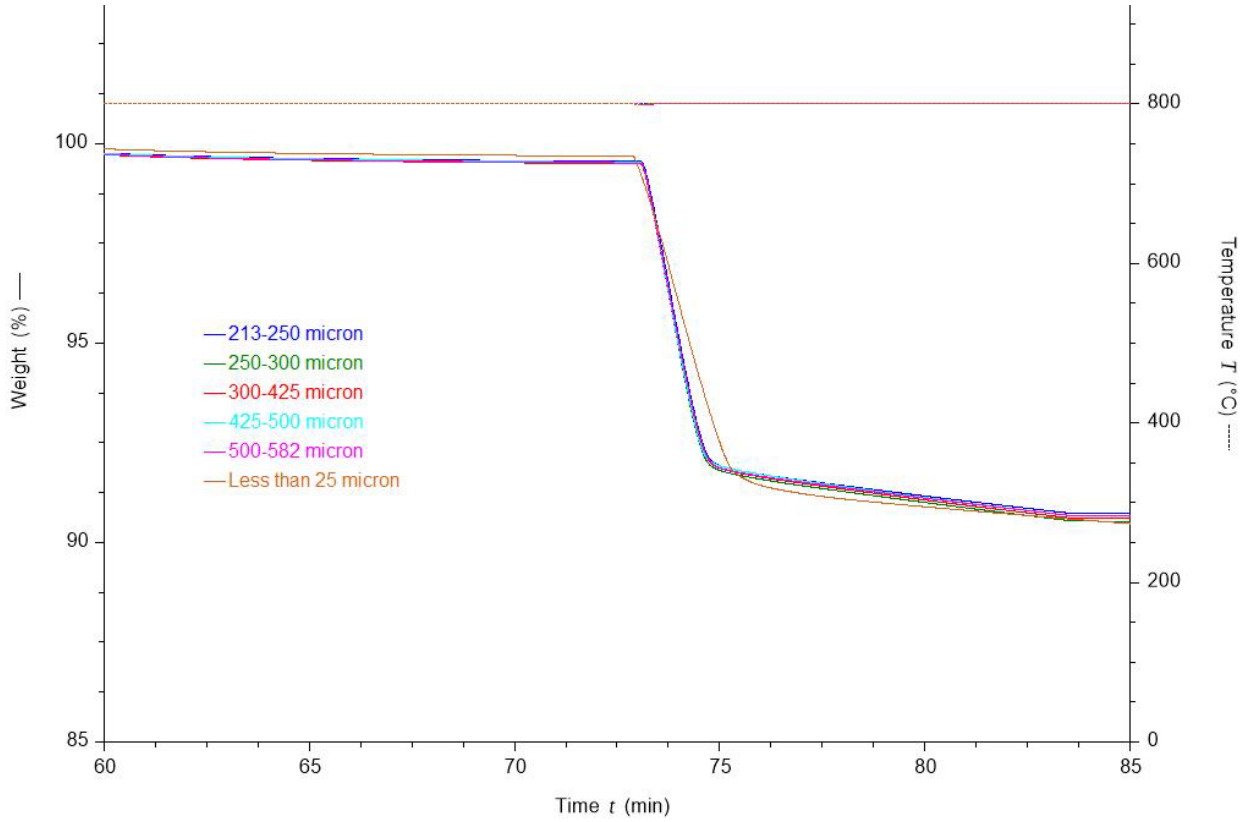


Fresh ***Reduced 10 min at 800°C***

- ***Surface morphology alters***
  - ***Pores arise in product layer 20-500 Angstroms***
  - ***Collective nodular phases of Cu^0***
  - ***Correlates with SA & Pore distribution findings***

Particle Size impact of reduction Behavior

TGA: 25-500 micron PS impact 20% H_2 @ 800°C



- **Prevalence of diffusion controlled regime resides in particle sizes 25-582 micron**
- **Particle size does not impact rate of conversion and presence of diffusion controlled regime**
- **Regime influenced by individual granular complexes**

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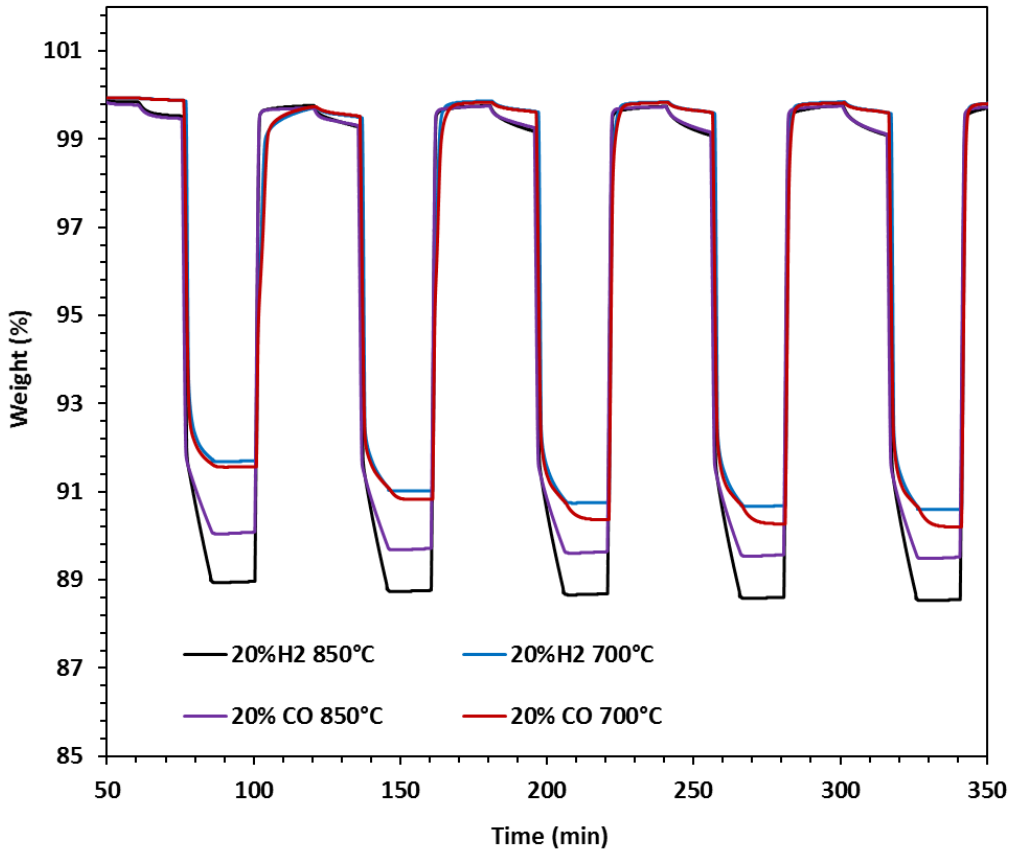
  - Thermogravimetric Analysis
  - Reduction Pathway (Solid State Chemical Changes associated with O^{2-} extraction)
  - Physical properties (BCs & Const.)
  - Surface Morphology Changes due to reduction (SEM)
- **Kinetic Modeling**
  - Iso-conversional Techniques (Determination of Conversion dependent activation energy)
  - Model descriptions and comparisons between gas phase components
- **Summary**

$CuFeAlO_4$ OC – Impact of reducing gas at 700 & 850°C- *Comparative reactivity with CO and H_2*

TGA – Reducing gas and temperature effect

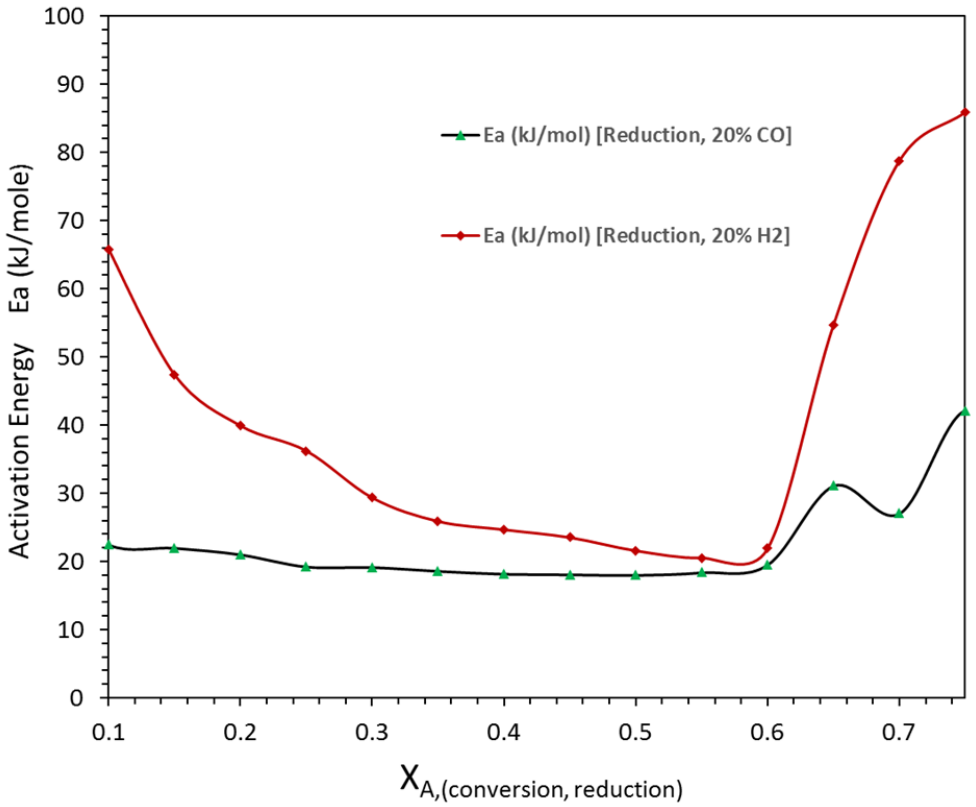
TG – 700 & 850°C



- Reactivity comparison
  - Temperature: 700°C
    - CO > H_2
  - Temperature: 750-850 °C
    - H_2 > CO
- Extent of reduction increases with rise in temperature (no sintering effects seen in this temperature range)
- *Range of temperatures used for extraction of activation energies*

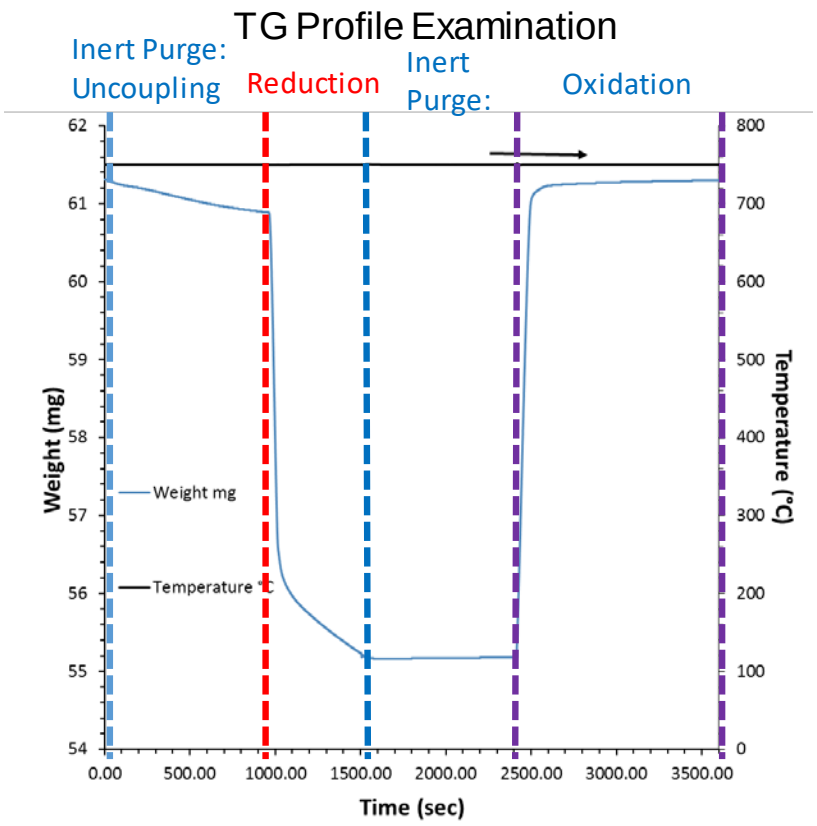
$CuFe_{2-x}Al_xO_4$ Pelletized OC – Overall Activation Energy Determination for CO & H_2

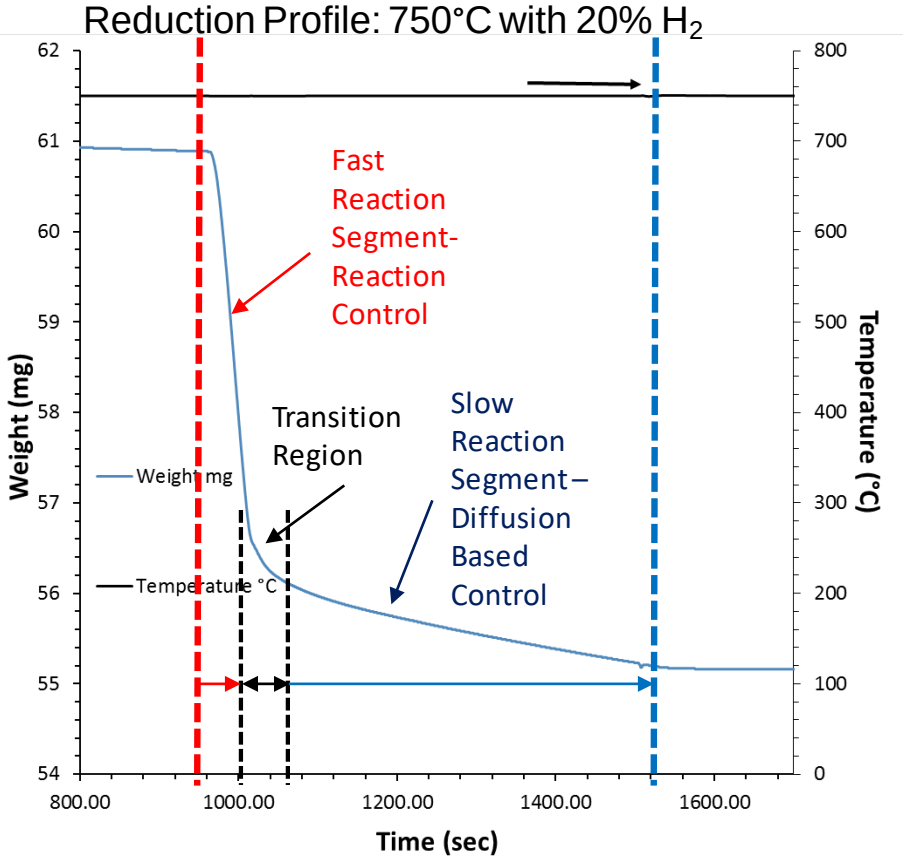
Reduction Activation Energy: Temperature Range 700-850°C



- *Overall Activation Energies determined through model free iso-conversional methods*
- $ln(t) = \left(-lnA + ln\int_0^X \frac{dX}{f(x)}\right) + \frac{E_a}{RT}$, *By plotting ln(t) with respect to 1/T for given value of* X_p *(Slope of regression line)*
- *Provides* E_a *as a function of* X_p*: Denoting possible controlling regime shifts*

$CuFe_{2-X}Al_XO_4$ Pelletized OC –Kinetic Particle Scale Representation Approach





- Reduction Reactions under consideration:
  - $5H_2 + 2CuFeAlO_4 \rightarrow 2Cu + 2Fe + Al_2O_3 + 5H_2O$
  - $5CO + 2CuFeAlO_4 \rightarrow 2Cu + 2Fe + Al_2O_3 + 5CO_2$
- Proposed Representation:
  - Series based mechanism bound by conversion limits. Transition from reaction control to diffusion based control. When one step ends the other begins denoted by a transition region solid conversion value, X_i.

$CuFeAlO_4$ Pelletized OC –Kinetic Particle Scale Representation Approach

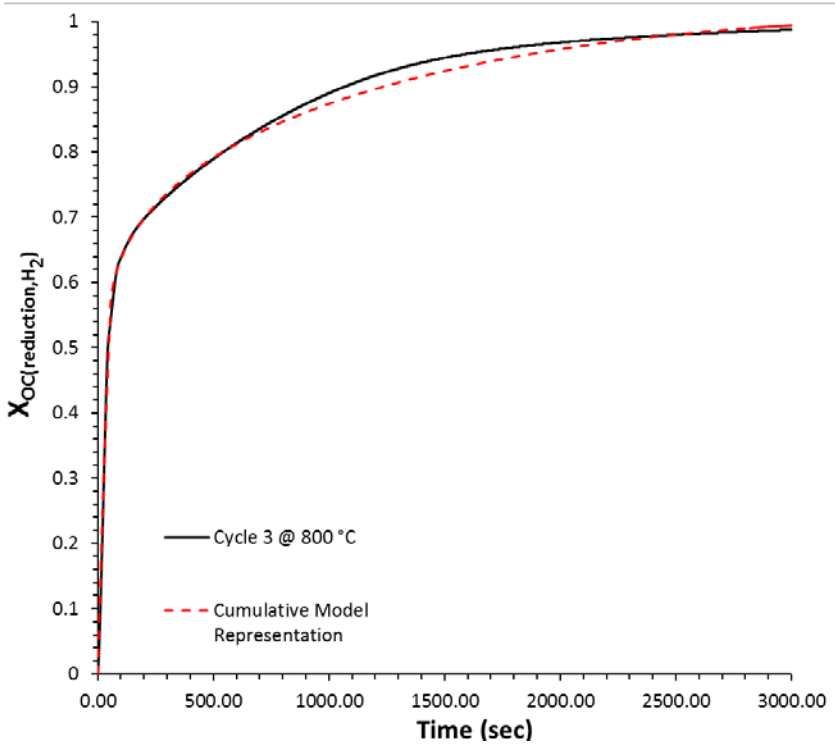
- Proposed Representation:
  - Series based reduction mechanism where reaction control and diffusion based control are represented by the Shrinking core model.
  - Shrinking Core model with reaction-diffusion resistances in series:
    - Kinetic-Reaction Controlled Reduction Segment:
      - $t = \tau_R \left(1 - \left(1 - X_p\right)^{\frac{1}{3}}\right) \qquad 0 \leq X_p \leq X_i$
    - Diffusion controlled Reduction Segment
      - $\mathrm{t} = \tau_D \left(1 - 3\left(\frac{1-X_p}{1-X_i}\right)^{\frac{2}{3}} + 2\left(\frac{1-X_p}{1-X_i}\right)\right) + \tau_R \left(1 - (1 - X_i)^{\frac{1}{3}}\right), \quad X_i \leq X_p \leq 1$
  - Series based mechanism is bound by conversion limits. When one step ends the other begins denoted by a transition region conversion value, X_i, Transition region occurring from ***0.4-0.6***
  - This representation is influenced by Park and Levenspiel's derivation of the Crackling core model

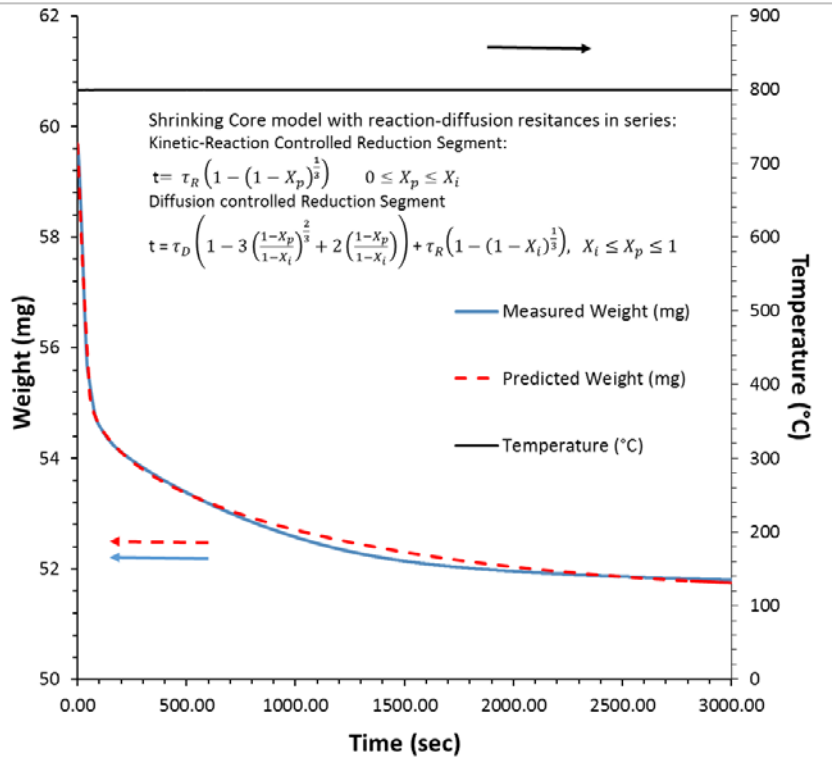
$CuFeAlO_4$ Pelletized OC –Kinetic Particle Scale Representation Approach cont.

- Proposed Representation (cont.):
  - Model Parameters:
    - $X_p = Oxygen\ Carrier\ conversion$
    - $\tau_R = \frac{\rho_B R_P}{b k''_{Ag} C^n_{Ag}}$
      - $\rho_B = particle\ density\ [g/cm^3]$
      - $R_P = mean\ particle\ radius\ [cm]$
      - $b = stoichiometric\ factor$
      - $k''_{Ag} = reaction\ rate\ constant\ [cm/s]$
      - $C^n_{Ag} = concentration\ of\ reactant\ in\ gas\ phase\ [g/cm^3]$, with $n = order\ of\ concentration\ dependence$
    - $\tau_D = \frac{\rho_B R_P^2}{6 b D_{e,Ag} C^n_{Ag}}$
      - $D_{e,Ag} = effective\ diffusivity\ of\ reactant\ [cm^2/s]$
    - $X_i = Transition\ region\ conversion\ value$

$CuFeAlO_4$ Pelletized OC –Kinetic Particle Scale Representation: H_2

Complete Reduction Representation with 20%H_2 @ 800°C, 60 min reduction



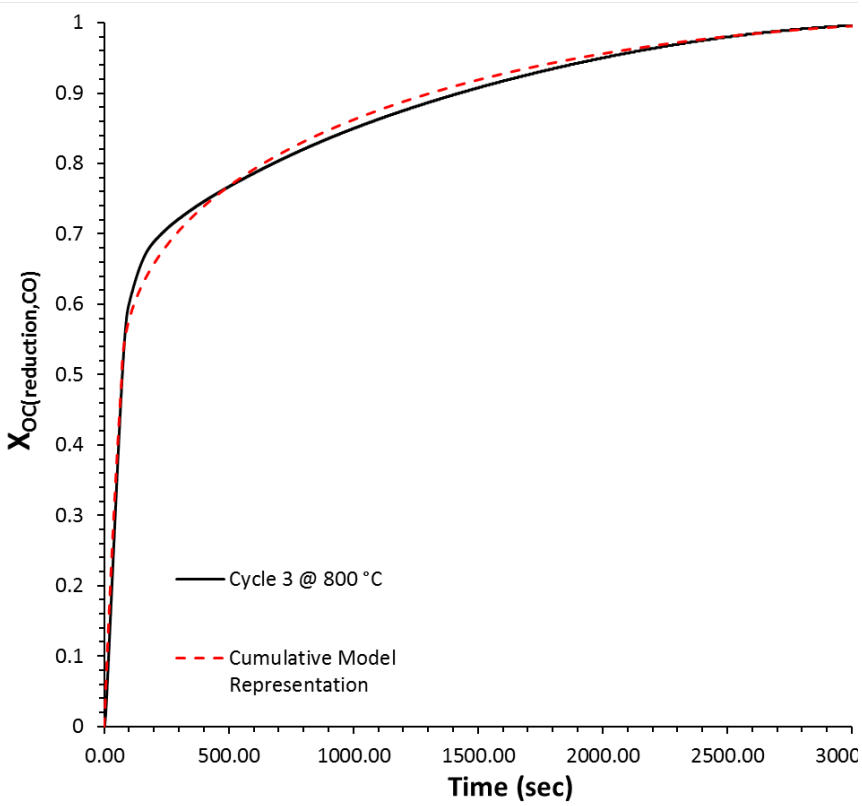


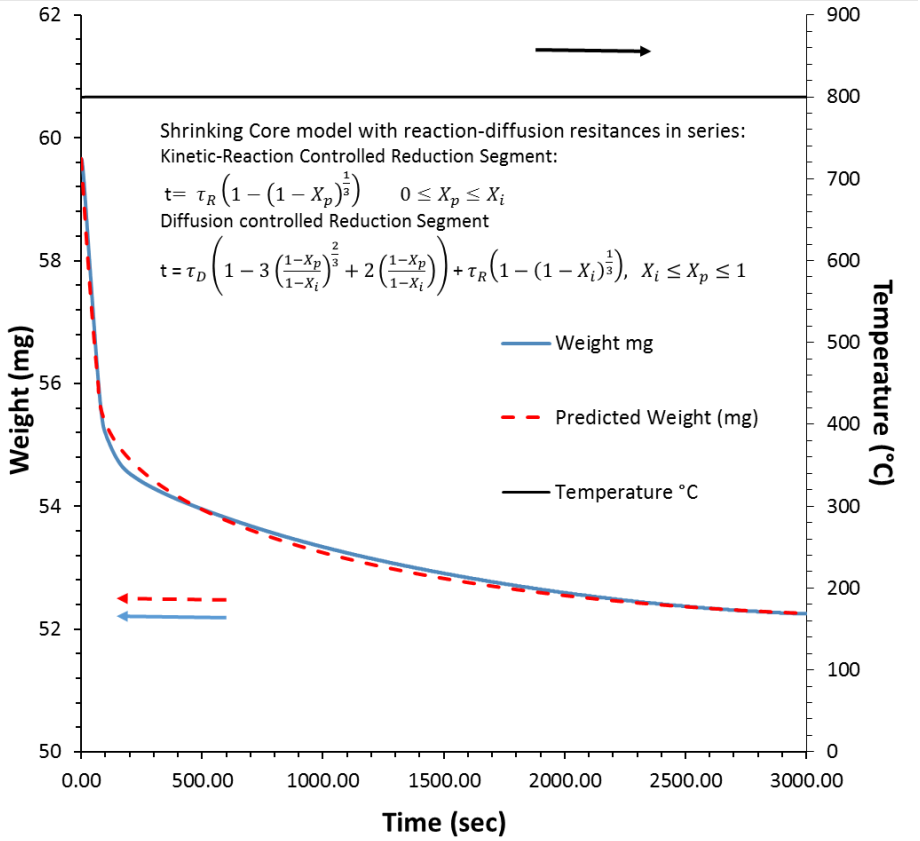
- k''_{H2}(800°C) = 0.068 [cm/s]
- $D_{e,H2}$(800°C) = 5.80E-6 [cm²/s]
- Based on model: $t(X_p = 0.5\,, @800°C\ with\ 100\%H_2) = 13.16\ sec$
  - $X_p = 0.5,\ OTC = 6.65\ wt\%\ transferable\ oxygen$

- R^2=0.986

$CuFeAlO_4$ Pelletized OC –Kinetic Particle Scale Representation: CO

Complete Reduction Representation with 20%CO @ 800°C, 60 min reduction





- $k_{CO}^{"}(800°C) = 0.032$ [cm/s]
- $D_{e,CO}(800°C) = 2.88E\text{-}07$ [cm²/s]
- Based on model: $t\left(X_p = 0.5\,, @800°C\ with\ 100\%CO\right) = 14.2\ sec$
  - $X_p = 0.5, OTC = 6.65\ wt\%\ transferable\ oxygen$

Summary

- **$CuFeAlO_4$ OC reduction pathway uncovered through coupling of TGA- ambient temperature XRD and In-Situ XRD**
  - **Phase distribution link to model**
- **Showed that key assumptions for the Simplified Grainy Pellet (SCM) model can be applied for the $CuFeAlO_4$ OC**
- **Application of a series based SCM provided an accurate means to describe reduction behavior**
- **Experimentally observed phenomena support model selection**
  - *Initial fast reaction controlled step followed by a diffusion controlled step*
  - $k''_{H_2} > k''_{CO}$ and $D_{e,H_2} > D_{e,CO}$

Future Work

- **Refinement of grain size distribution for application in model:**
  - **XRD & Rietveld Refinement**
- **Application of derivations that incorporate grain shapes other than spherical**
- **Application of non-isothermal models to incorporate:**
  - ΔH_{rxn}
  - **Explore ΔT in particle**

Acknowledgements

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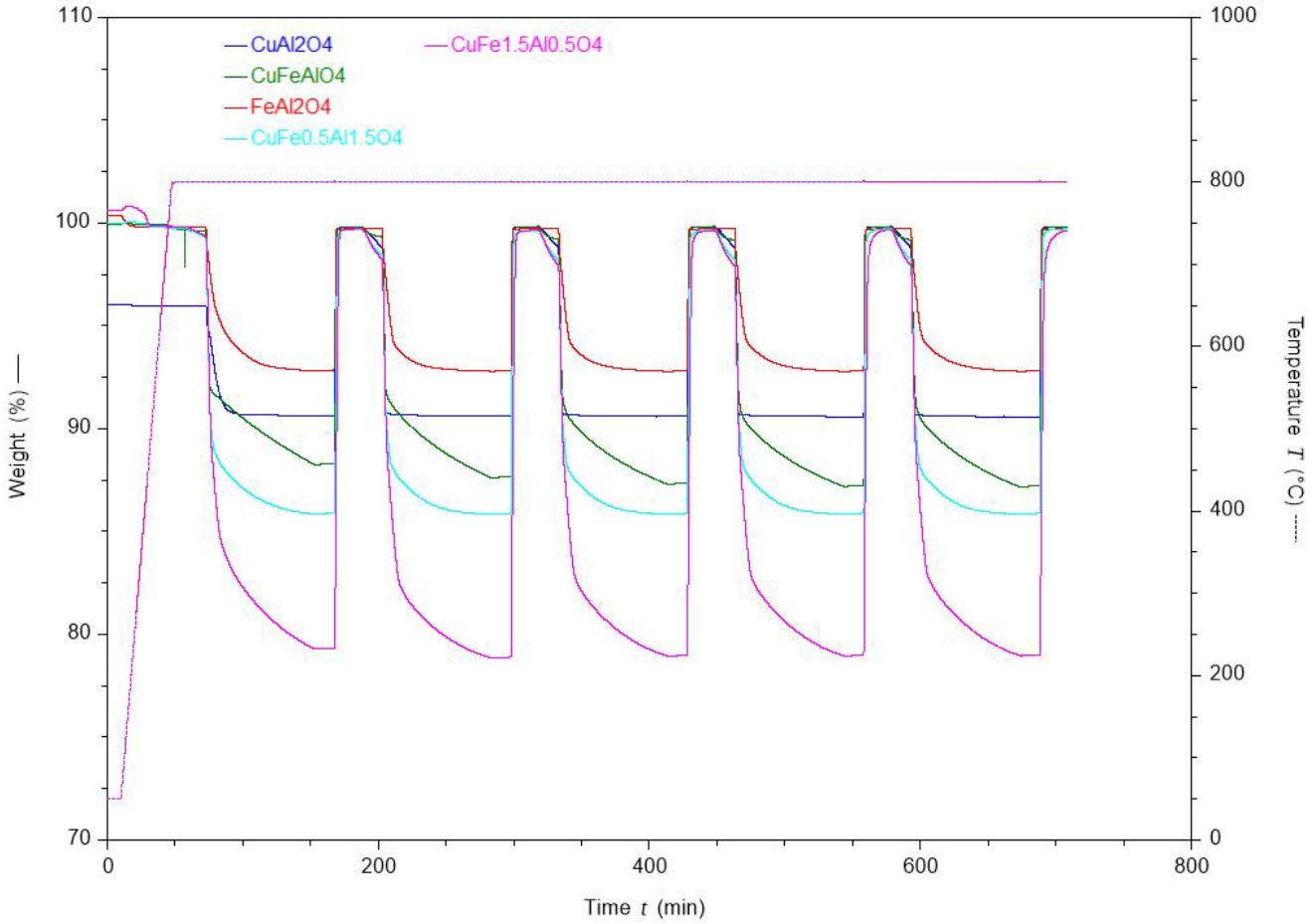
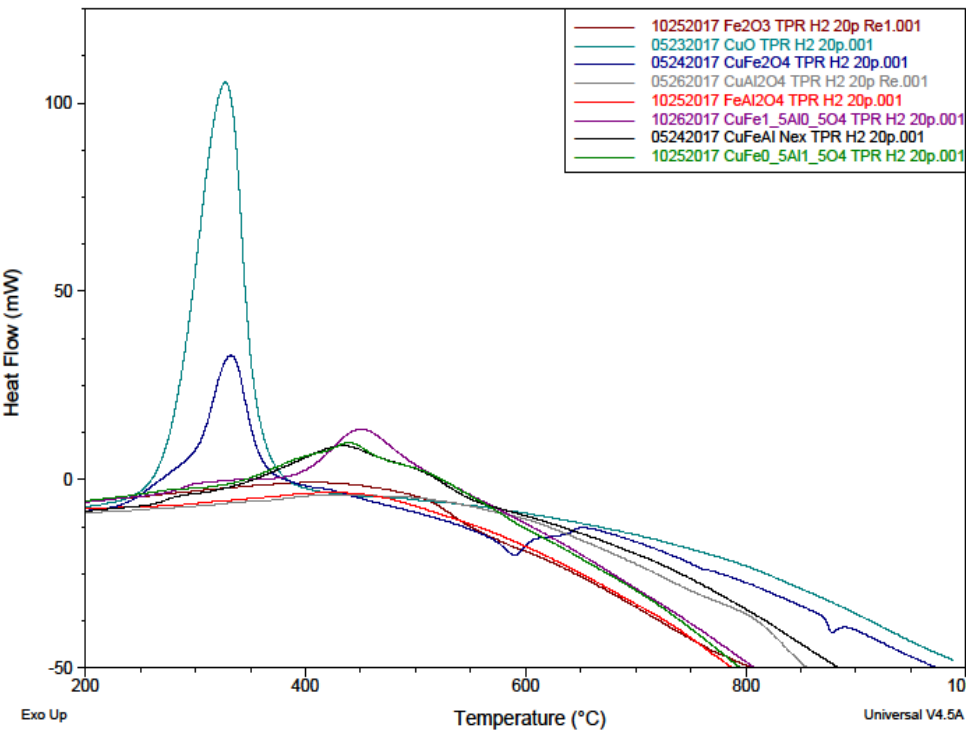
TGA Comparison of Spinel Aluminates

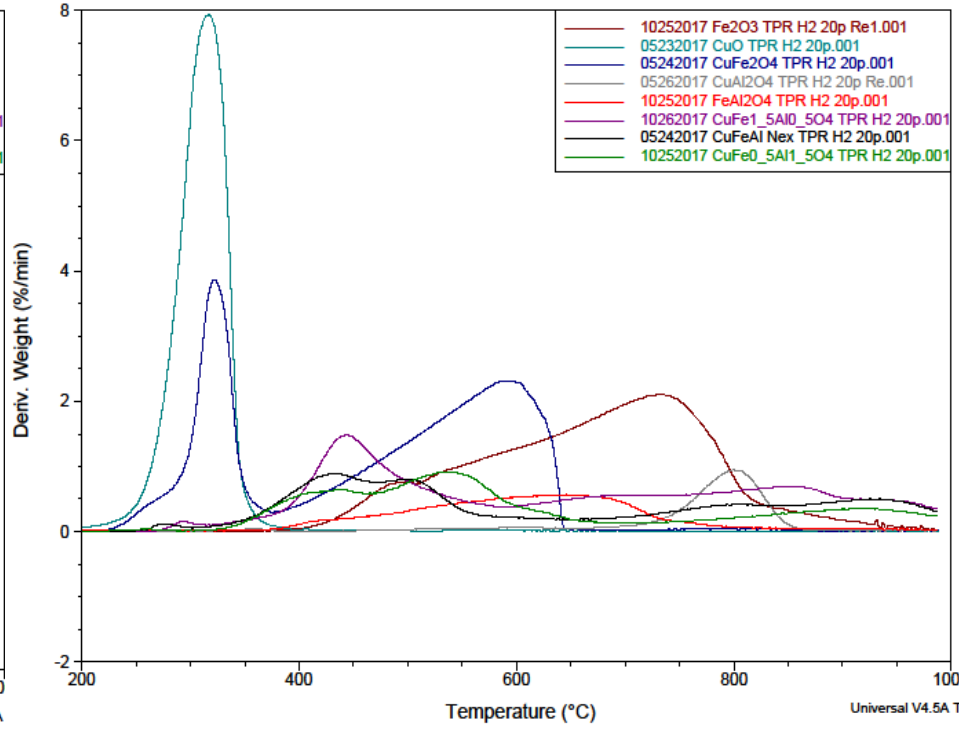


- Fe-aluminate reducible with H_2
- Does not exhibit same rate as diffusion controlled regime in $CuFeAlO_4$
- Slowing of oxygen transfer rate is not solely dependent up reduced material presence

Thermochemical differentiation (TGA-DSC)

Using Characteristic Heat Flow measurements for Component differentiation





Heat Flow ***Reduction Rate***

- **Characteristic Heat flow curves can be used to differentiate metal oxides with close lattice structure**
  - Provides support of XRD findings for primary phase
  - $CuFeAlO_4$ unique in comparison to base metal oxides and bi-tri metallic variants
- **Provides indication of exo/endothermicity**