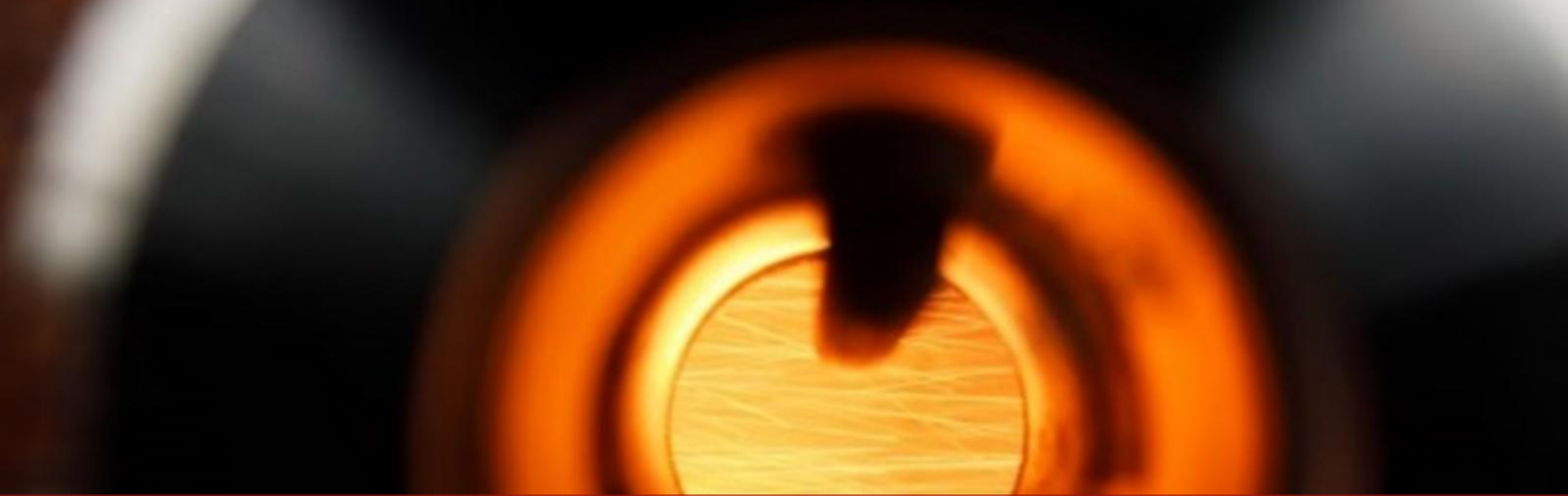


The unique problems of iron-dust combustion and its applications

DCSI WEBINAR, FRIDAY FEBRUARY 24, 2023, 13:00-14:00 CET

Xiaocheng Mi (assistant professor)

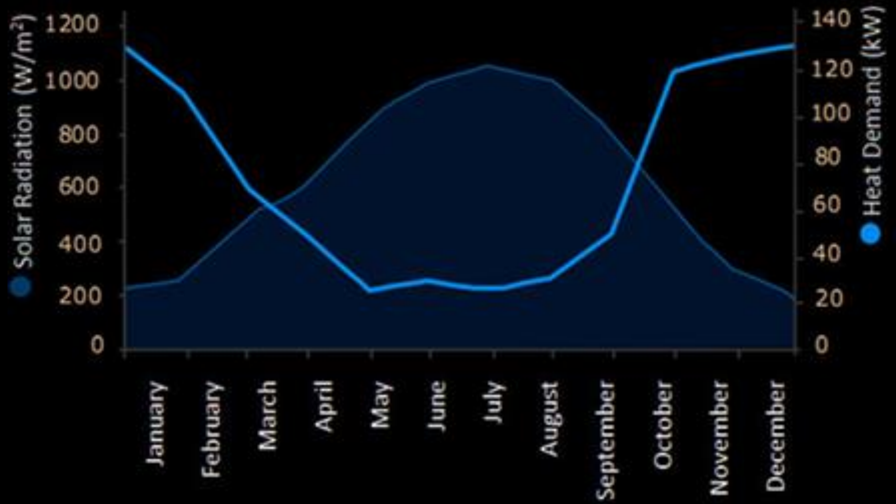
Mechanical Engineering, Power & Flow

EIRES EINDHOVEN INSTITUTE FOR RENEWABLE ENERGY SYSTEMS

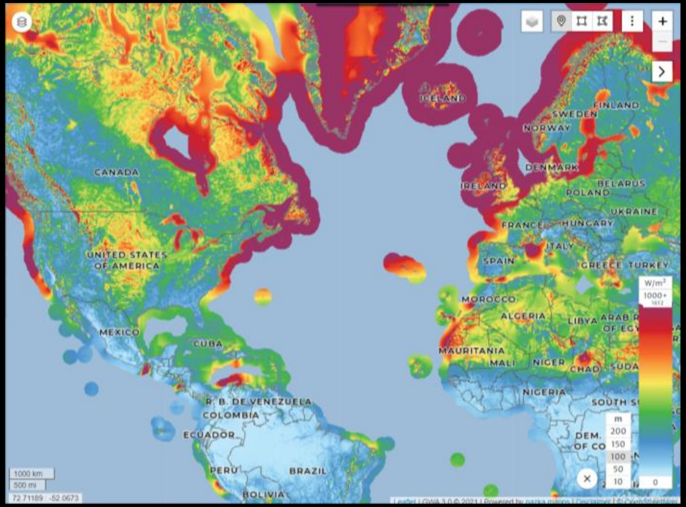
TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Power generated by renewable sources is *intermittent* and *geographically scattered*.

Solar radiation vs. heat demand in the NL



Map of wind power density (WPD)



Global Wind Atlas: http://www.globalwindatlas.inf

Supply ≠ Demand in time and space

Supply ≠ Demand in time and space

How to efficiently ***store*** and ***transport*** renewable energy?

↑ **Solution**

We need ***good*** energy carriers.

Criteria for good energy carriers to replace *carbon*

- Easy to release its chemical energy, reactive in air and/or water

- High specific energy, no heavy elements

- Not rare/expensive

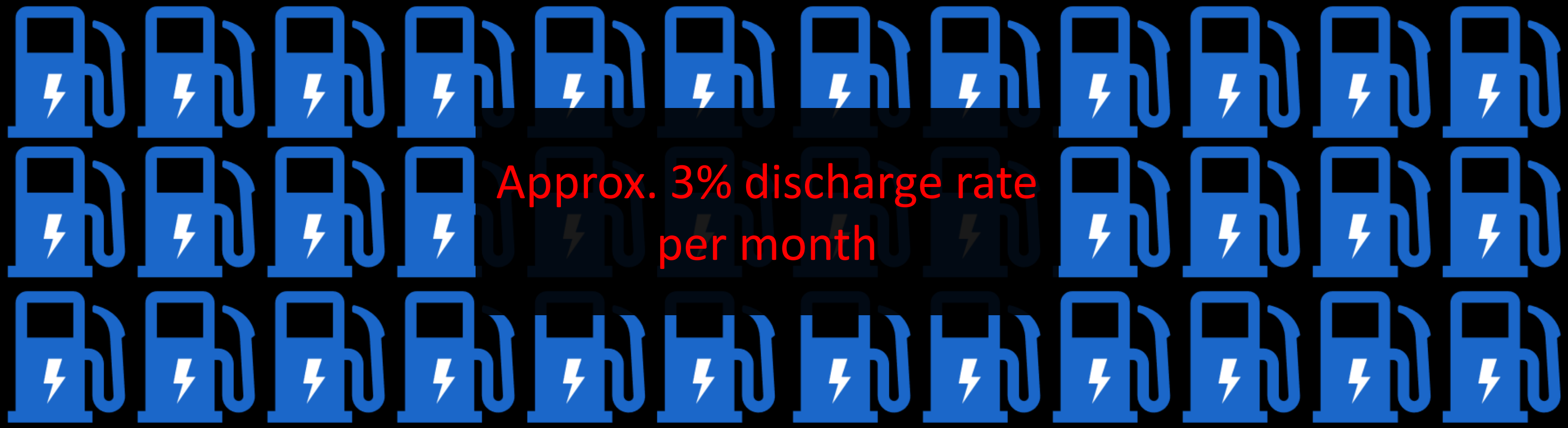
- Non-toxic

- Controllable oxidation/combustion

Hydrogen and Lithium-ion battery have their drawbacks…

Low energy densities

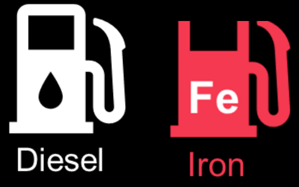
Fire and explosion hazards



Metal-enabled Cycle of *Renewable Energy* (MeCRE) using *iron dust*

Carbon-free

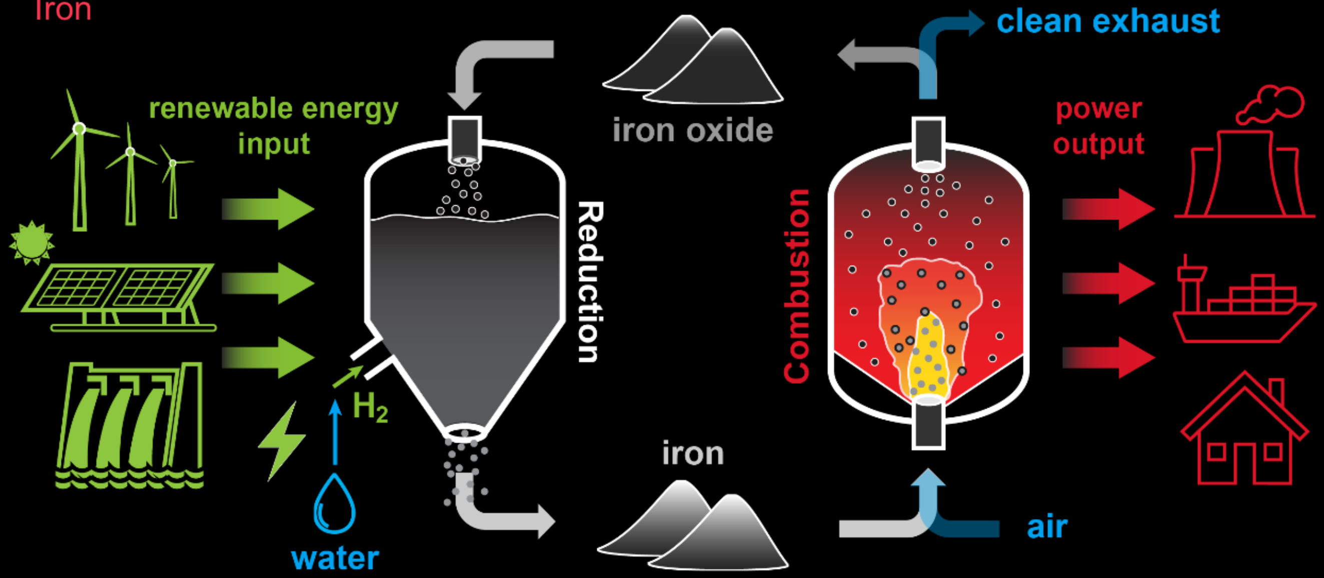
High energy density



Safe storage and transportation

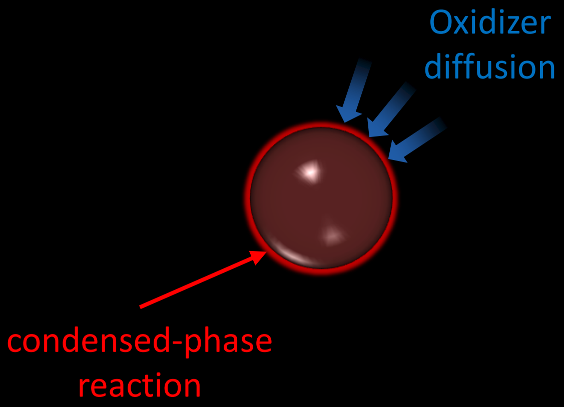
Negligible energy loss over seasonal storage

Potential to recycle nearly 100% of iron mass after combustion



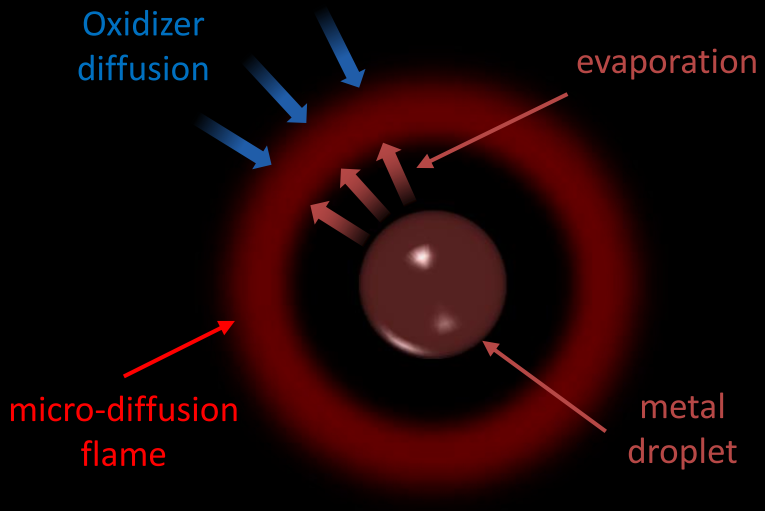
Iron-particle combustion is non-volatile

non-volatile combustion



metals with ***high*** melting and boiling points,
e.g., ***iron***

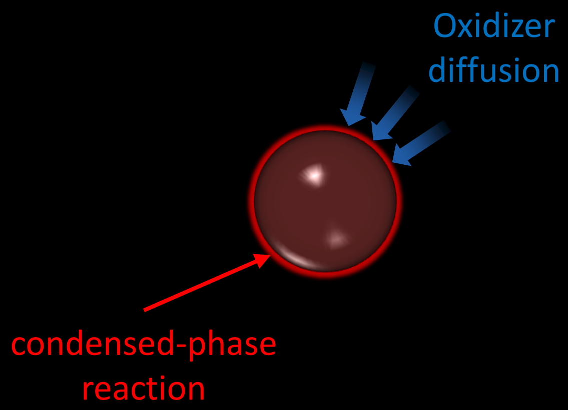
volatile combustion



metals with ***low*** melting and boiling points
e.g., aluminum, magnesium

Unique features of iron-particle combustion

non-volatile combustion

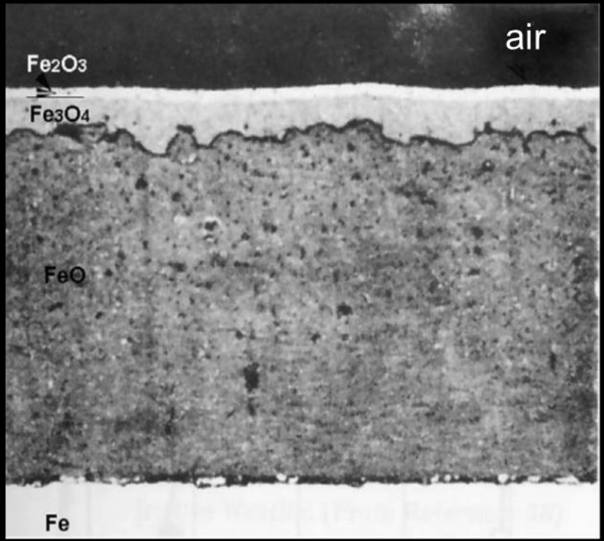


metals with ***high*** melting and boiling points,
e.g., ***iron***

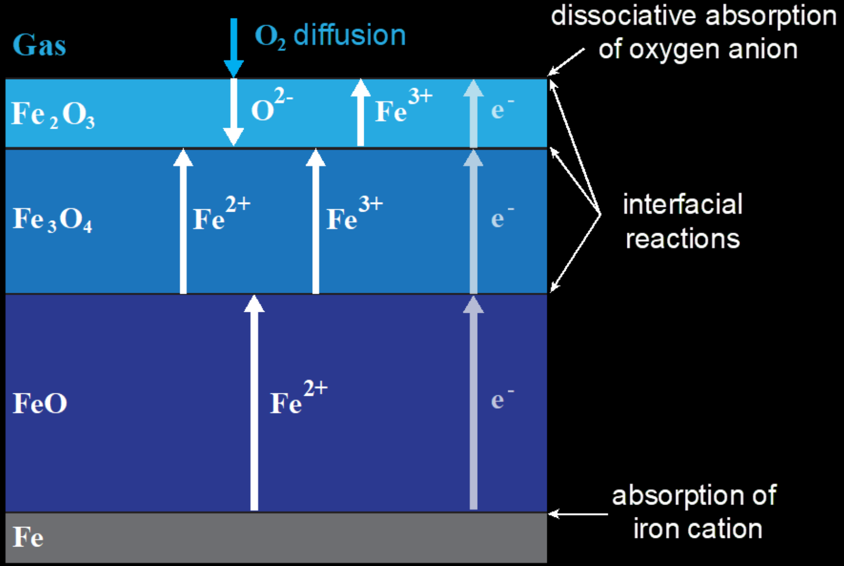
Unique features

- Heterogeneous oxidation processes
- Spatially discrete flame propagation behavior

Solid-phase iron oxidation



1% Fe_2O_3 (hematite)
4% Fe_3O_4 (magnetite)
95% FeO (wustite)

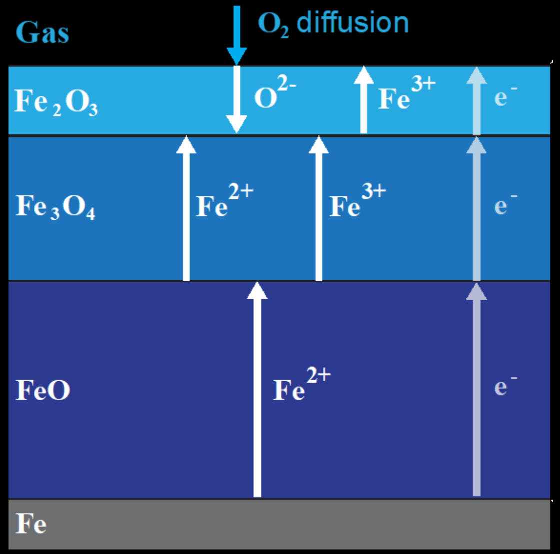


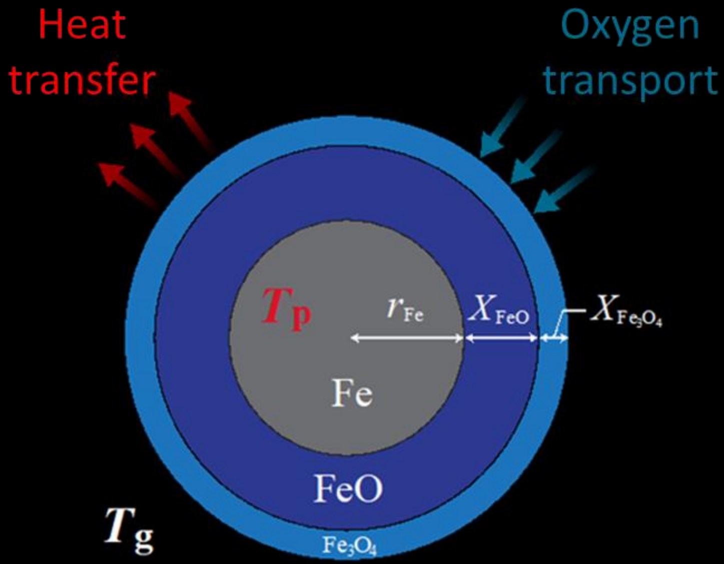
Formation of multiple compact layers of oxides

Fe ion diffusion through the layers is rate limiting.

Païdassi, J., 1958. Sur la cinetique de l'oxydation du fer dans l'air dans l'intervalle 700–1250° C. *Acta Metallurgica*, *6*(3), pp.184-194.

Ignition model for a single iron particle





Fe ion diffusion through the layers is ***rate limiting***.

Model based on ***solid-phase oxidation kinetics*** describes particle ***ignition***.

Mi, Fujinawa, and Bergthorson, 2022. A quantitative analysis of the ignition characteristics of fine iron particles. *Combustion and Flame*, 240, p.112011.

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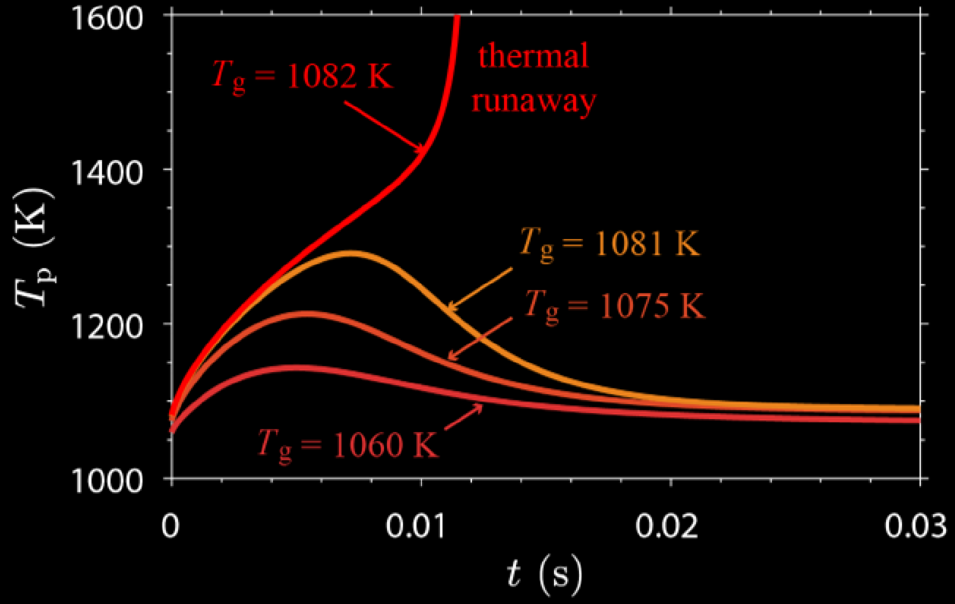
$\dot{q}_{\mathrm{release}} > \dot{q}_{\mathrm{loss}}$ → particle undergoes *thermal runaway*

Particle temperature T_p



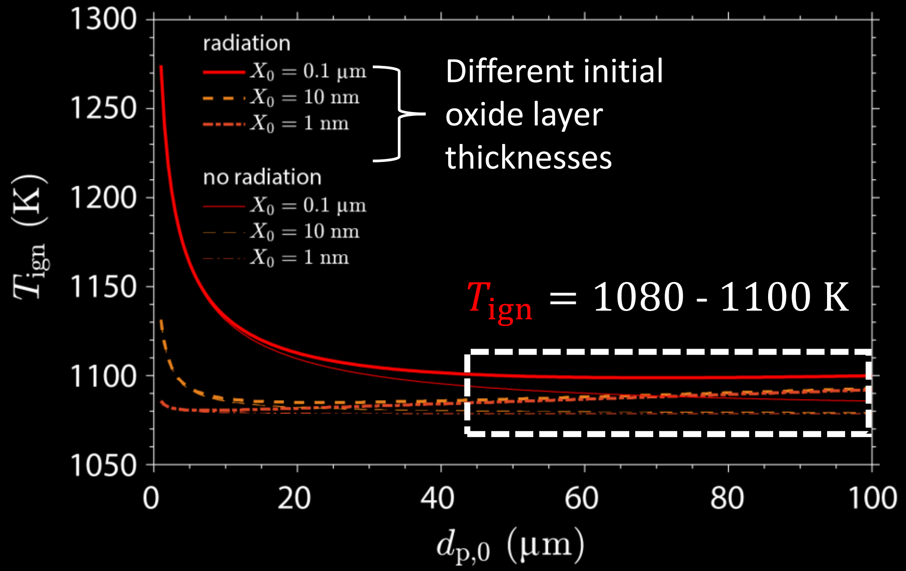
Minimum gas temperature T_g to trigger thermal runaway

⇩

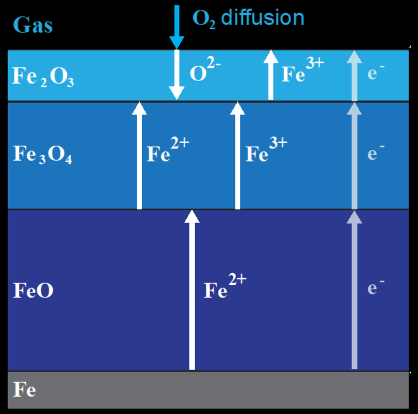
Ignition temperature T_{ign}

Mi, Fujinawa, and Bergthorson, 2022. A quantitative analysis of the ignition characteristics of fine iron particles. Combustion and Flame, 240, p.112011.

Model prediction of T_{ign} and open questions



Compact oxide layer assumption



➡ T_{ign} plateaus as $d_{p,0}$ increases

➡ T_{ign} independent of O_2 concentration

	T_{ign} (K)	Specimen	Conditions
Grosse & Conway, exp.	1203 ± 10	10-g-weighted iron	Flow of O_2 at 1 atm
Bolobov, exp.	1233 ± 20	5 × 5 × 0.5 mm low-carbon steel foil	O_2 at 0.14-0.6 MPa

Experimental verification is required!

Mi, Fujinawa, and Bergthorson, 2022. A quantitative analysis of the ignition characteristics of fine iron particles. Combustion and Flame, 240, p.112011.

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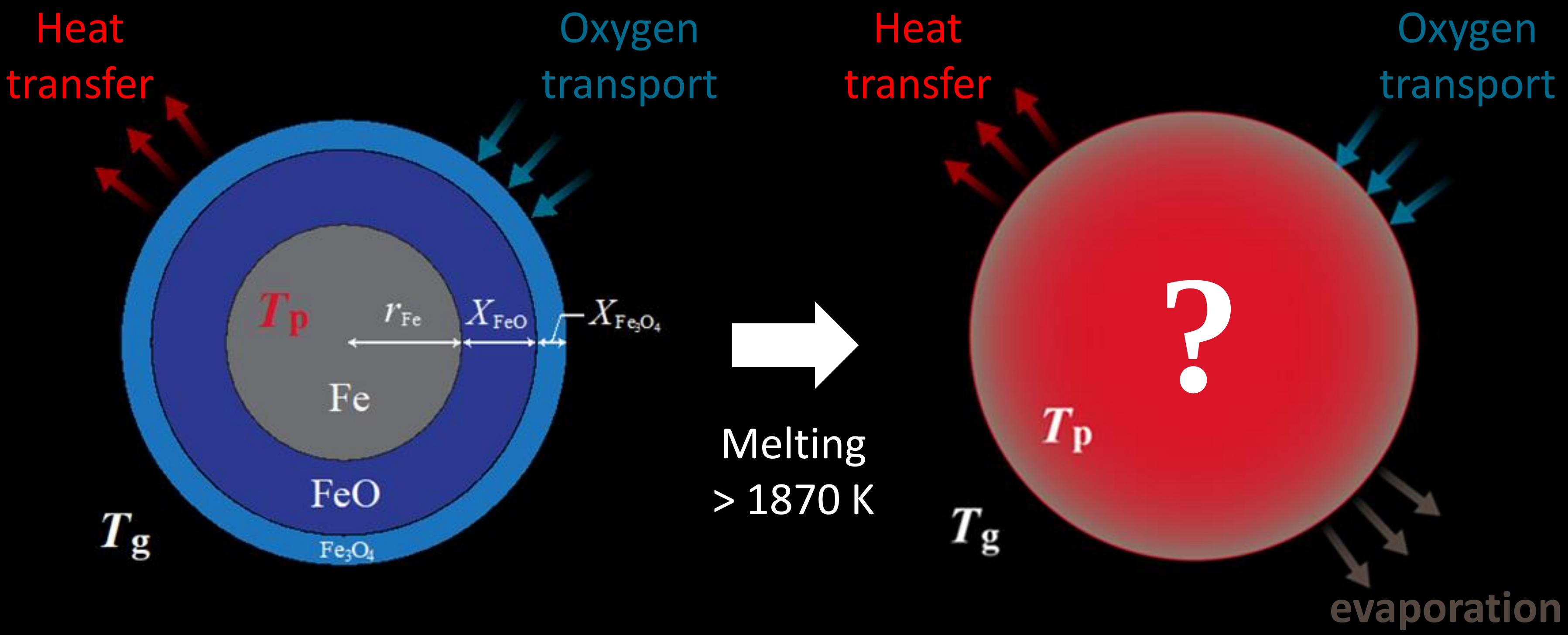
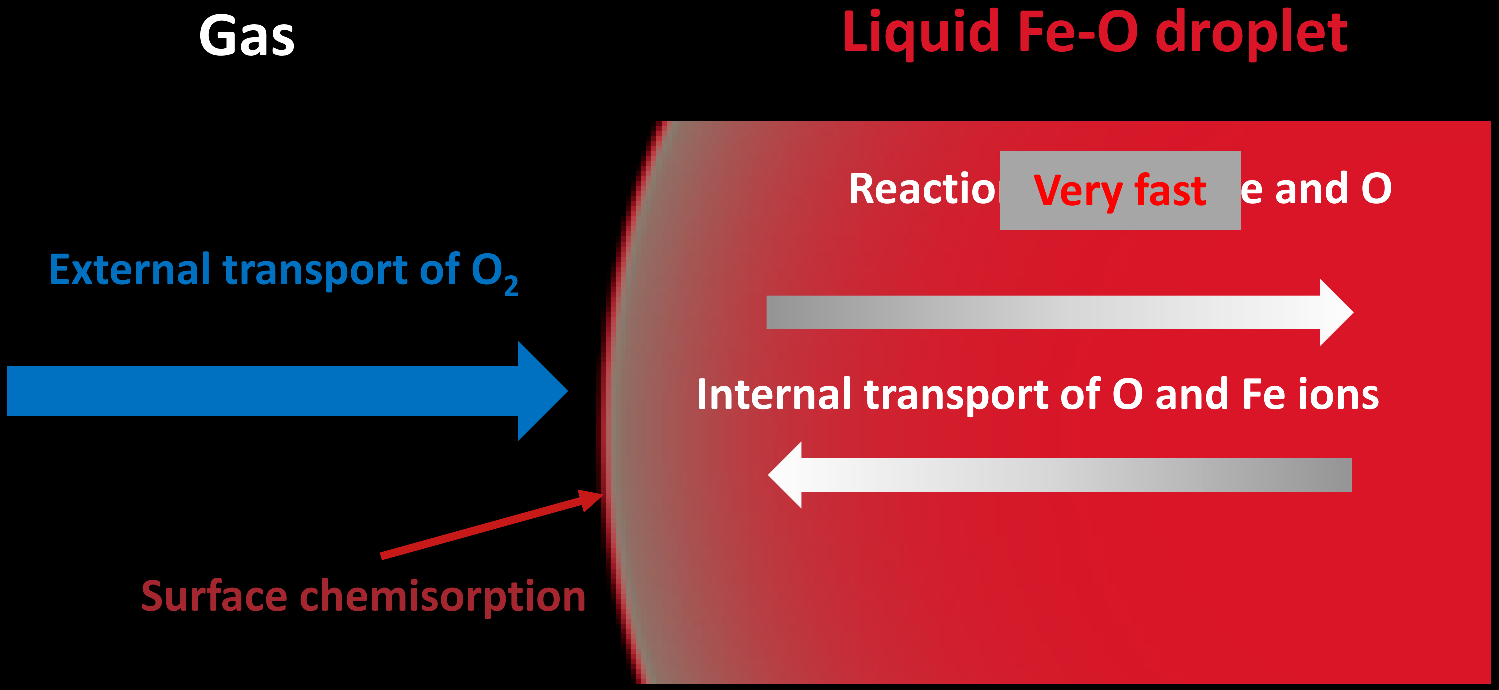
Liquid iron oxidation is poorly known

Solid particle | Molten droplet



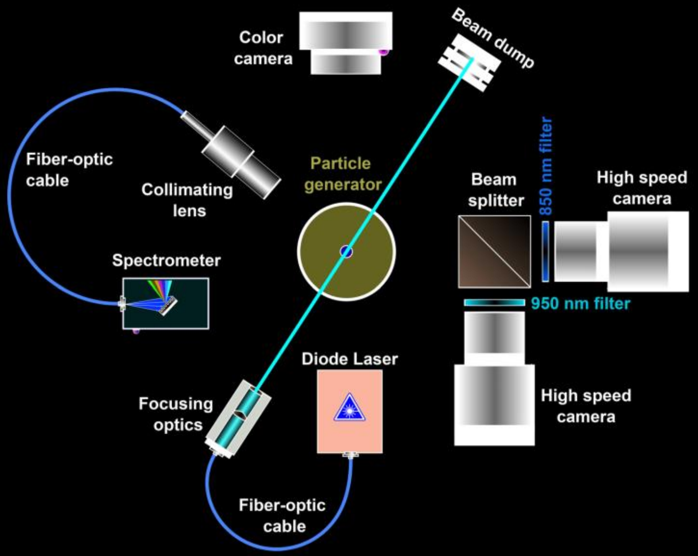
What is the limiting factor(s) of heat release rate?



External transport, surface chemisorption, internal transport, or an interplay?

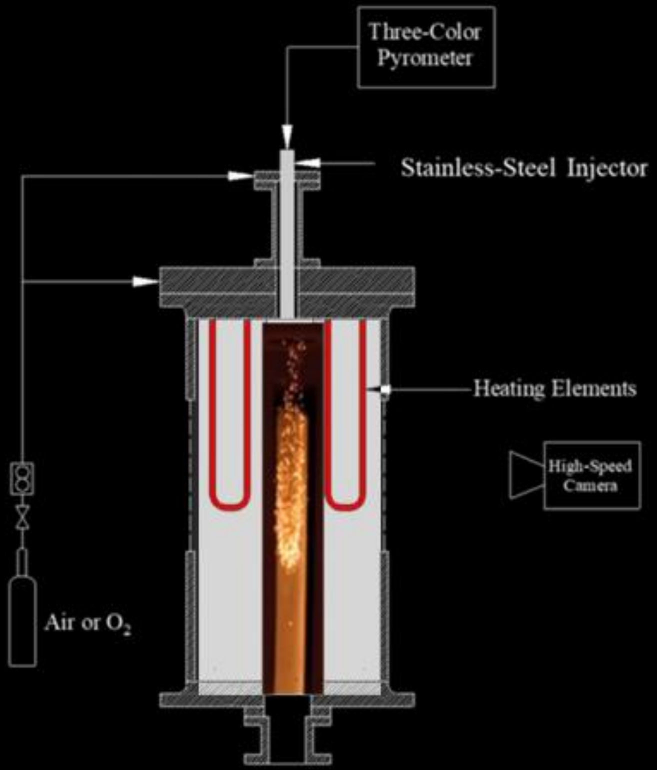
Experimental measurement for single-Fe combustion

Laser-ignited particle burning in air at room temperature by Ning *et al*. (2021)



Ning, D., Shoshin, Y., van Stiphout, M., van Oijen, J., Finotello, G. and de Goey, P., 2022. Temperature and phase transitions of laser-ignited single iron particle. *Combustion and Flame*, *236*, p.111801.

Particle burning in a drop tube at 1350 K with various O_2 concentrations by Panahi *et al*. (2022)

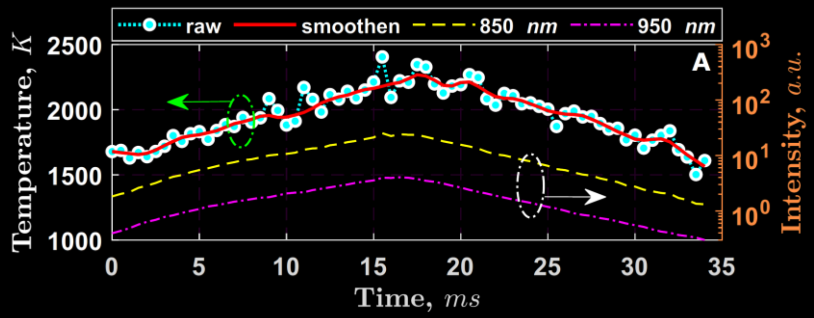


Panahi, A., Chang, D., Schiemann, M., Fujinawa, A., Mi, X., Bergthorson, J.M. and Levendis, Y.A., 2023. Combustion behavior of single iron particles-part I: An experimental study in a drop-tube furnace under high heating rates and high temperatures. *Applications in Energy and Combustion* Science, 13, p.100097.

Experimental measurement for single-Fe combustion

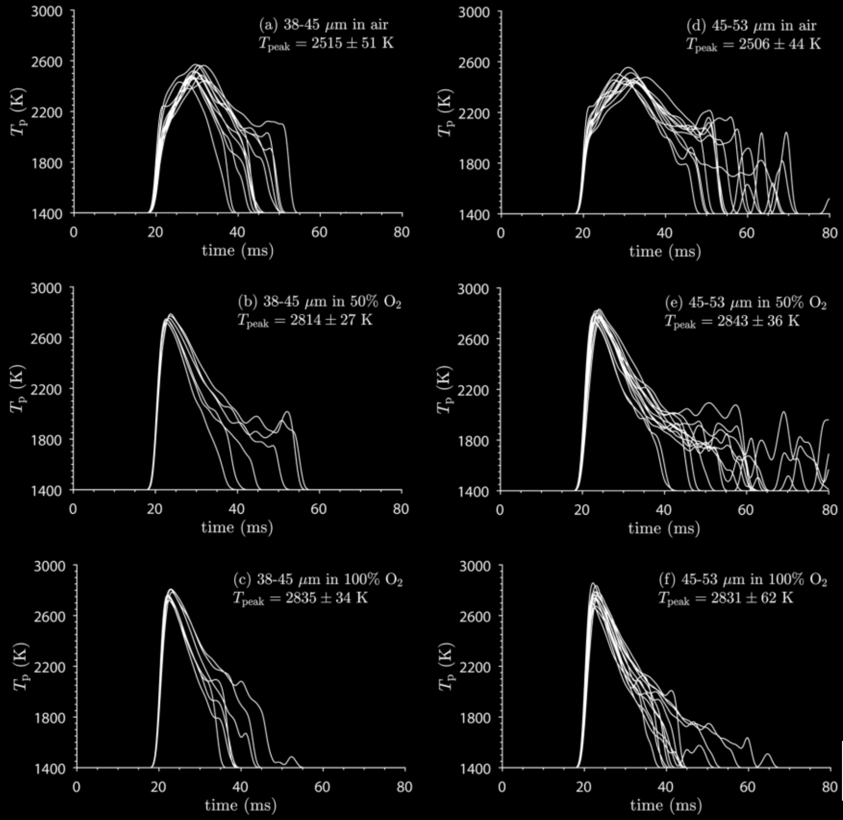
Laser-ignited particle burning in air at room temperature by Ning *et al*. (2021)

Mean particle size = 54 µm



Ning, D., Shoshin, Y., van Stiphout, M., van Oijen, J., Finotello, G. and de Goey, P., 2022. Temperature and phase transitions of laser-ignited single iron particle. *Combustion and Flame*, *236*, p.111801.

Particle burning in a drop tube at 1350 K with various O_2 concentrations by Panahi *et al*. (2022)

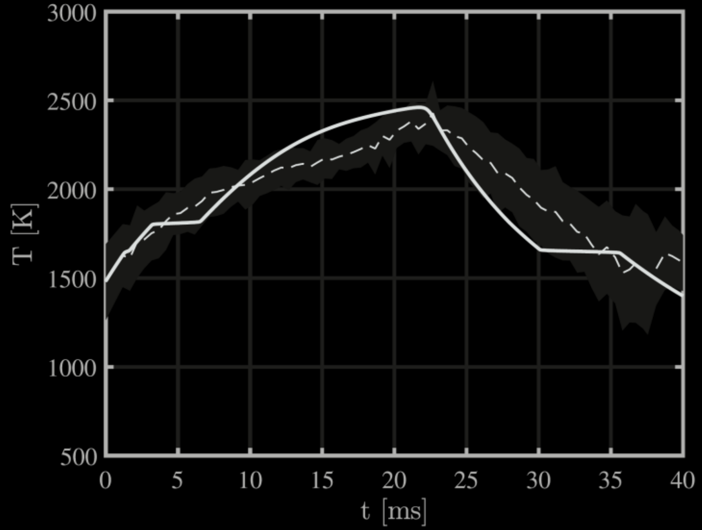


Panahi, A., Chang, D., Schiemann, M., Fujinawa, A., Mi, X., Bergthorson, J.M. and Levendis, Y.A., 2023. Combustion behavior of single iron particles-part I: An experimental study in a drop-tube furnace under high heating rates and high temperatures. *Applications in Energy and Combustion* Science, 13, p.100097.

An early campaign of Fe-particle combustion modeling

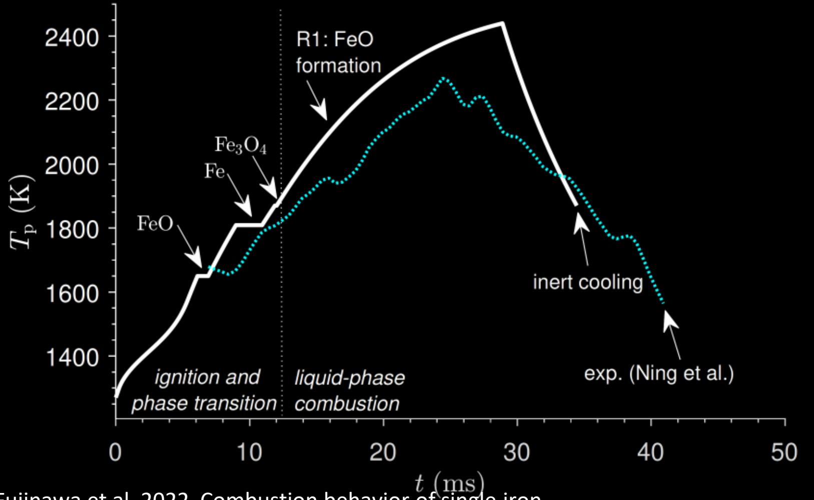
Assuming:
- Infinitely fast internal transport
- Liquid FeO is the only product (no further oxidation)
- 100% surface absorption of O_2 until fully converted to FeO
- Heat and mass transfer in the boundary layer is in a continuum regime

Boundary-layer resolved model by Thijs *et al*. (2022)



Thijs et al., 2022. Resolved simulations of single iron particle combustion and the release of nano-particles. *Proceedings of the Combustion Institute*.

Zero-dimensional single-particle model by Fujinawa *et al*. (preprint, 2022)



Fujinawa et al. 2022. Combustion behavior of single iron particles—Part II: A theoretical analysis based on a zero-dimensional model. (Under review) *Appl Energy Combust Sci*.

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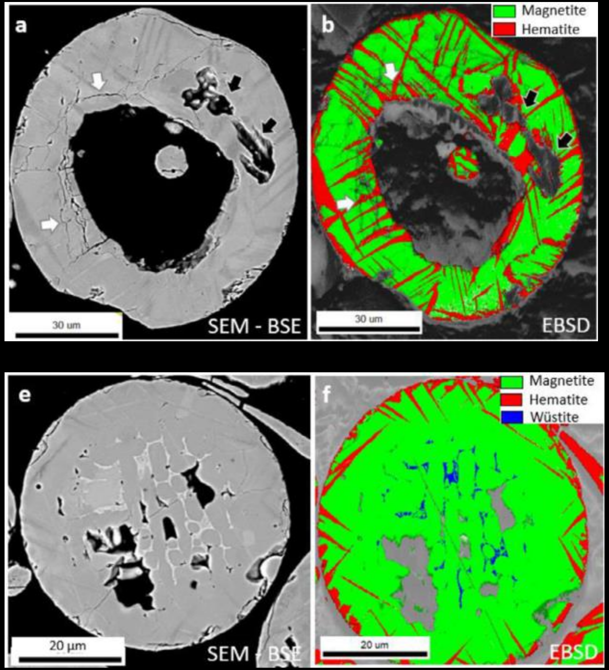
Experimental evidence showing further oxidation beyond FeO



Magnetite: Fe_3O_4
Hematite: Fe_2O_3
Wustite: FeO

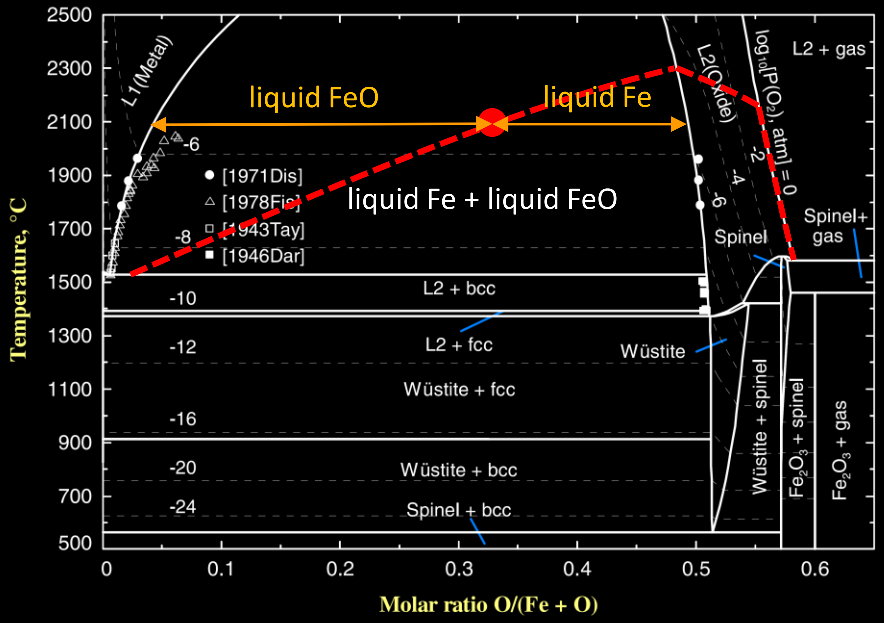
SEM: Scanning electron microscope

BSE: Backscattering electrons

EBSD: Electron backscatter diffraction

Choisez *et al*. (2022), Phase Transformations and Microstructure Evolution During Combustion of Iron Powder. Preprint available at SSRN 4080963..

Phase diagram based on thermochemical equilibrium calculation



Hidayat, T., Shishin, D., Jak, E. and Decterov, S.A., 2015. Thermodynamic reevaluation of the Fe–O system. *Calphad*, 48, pp.131-144.

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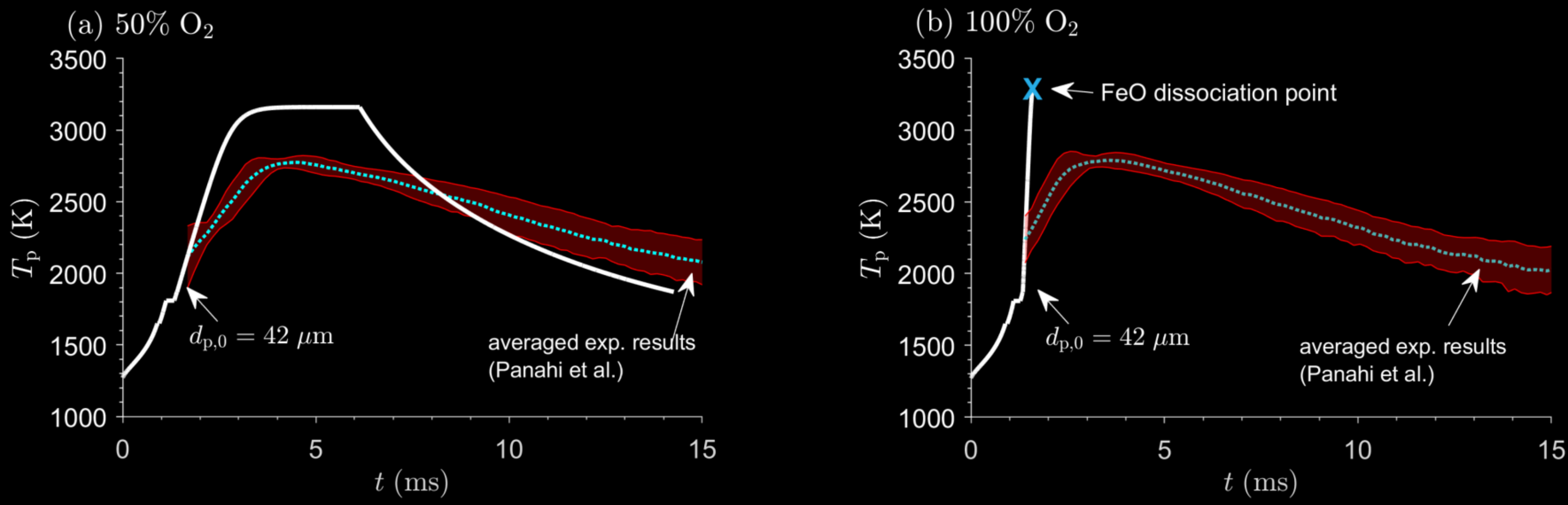
Early models fail to capture Fe-combustion in higher O_2 environments



Fujinawa et al. 2022. Combustion behavior of single iron particles—Part II: A theoretical analysis based on a zero-dimensional model. (Under review) *Appl Energy Combust Sci.*

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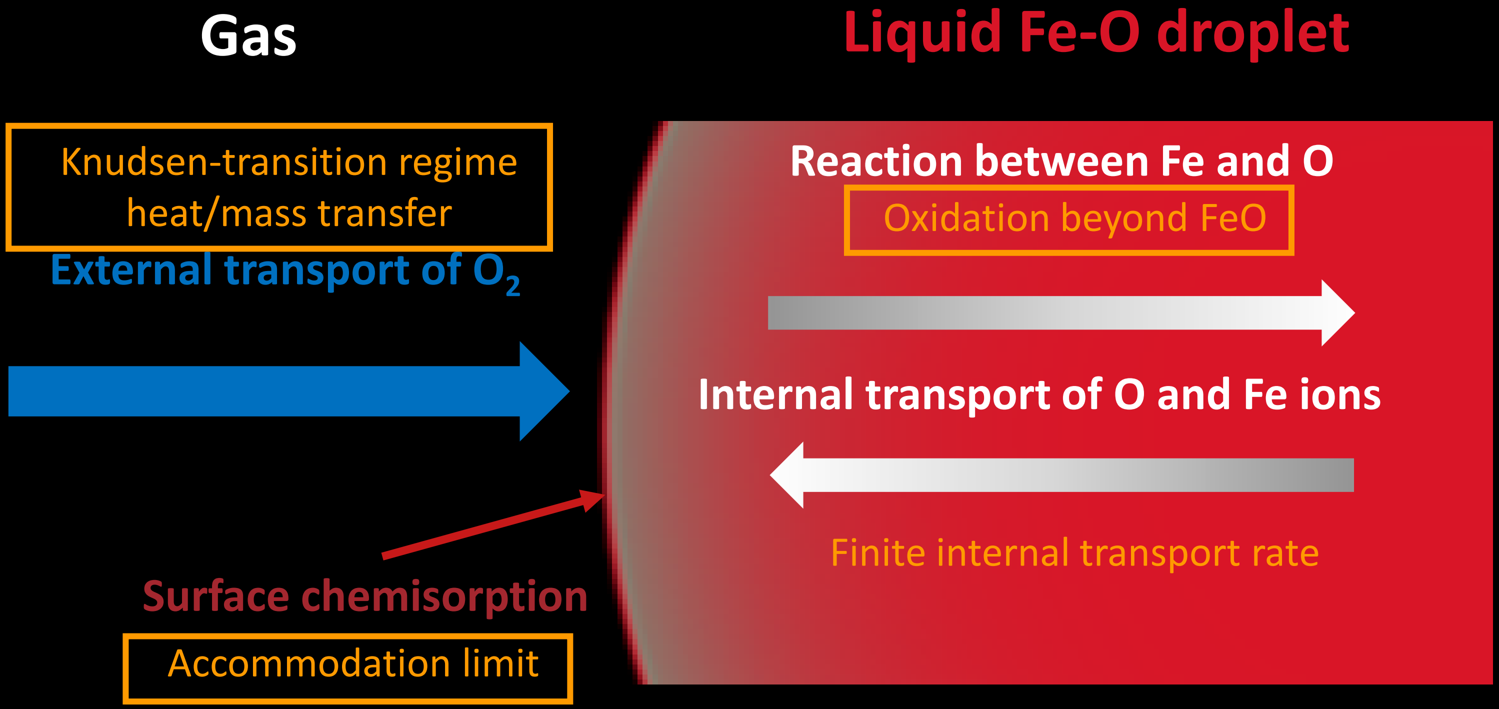
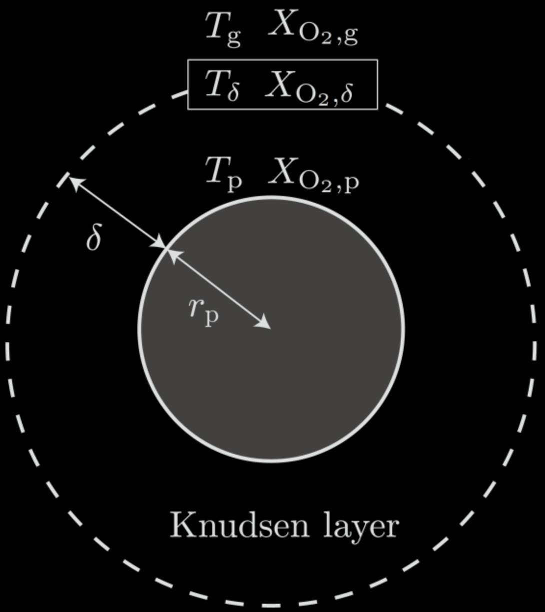
What are the missing physics?



Knudsen transition regime of heat and mass transfer

Two-layer model



Knudsen layer thickness
=
Gas-phase molecular mean free path

Outside the Knudsen layer: Continuum heat/mass transfer
Inside the Knudsen layer: Free-molecular heat/mass transfer

Mass transfer rate:

$$\dot{m}_{O_2,FM} = \alpha_m \pi r_p^2 v_\delta \rho_{O2,\delta} X_{O_2,\delta}$$

Heat transfer rate:

$$q_{FM} = \alpha_T \pi r_p^2 p \sqrt{\frac{k_b T_\delta}{8\pi m_{O_2}}} \frac{\gamma^* + 1}{\gamma^* - 1} \left(\frac{T_p}{T_\delta} - 1 \right)$$

Mass accommodation coefficient (MAC):

$$\alpha_m = \frac{n_{abs,g}}{n_{tot,g}}$$

Thermal accommodation coefficient (TAC):

$$\alpha_T = \frac{\langle E_0 - E_i \rangle}{3k_B (T_s - T_g)}$$

Thijs, L.C., Kritikos, E., Giusti, A., Ramaekers, W.J., van Oijen, J.A., de Goey, L.P. and Mi, X.C., 2022. On the combustion of fine iron particles beyond FeO stoichiometry: Insights gained from molecular dynamics simulations. arXiv preprint arXiv:2212.06432.

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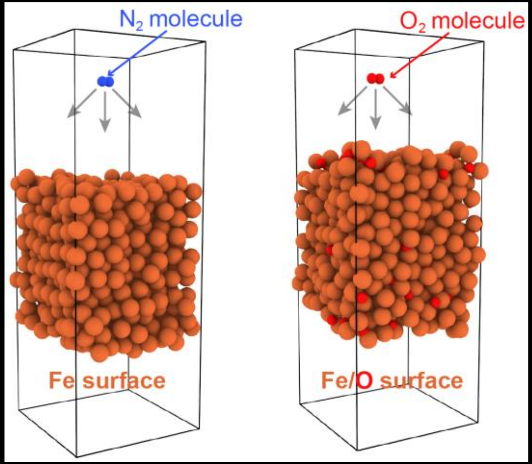
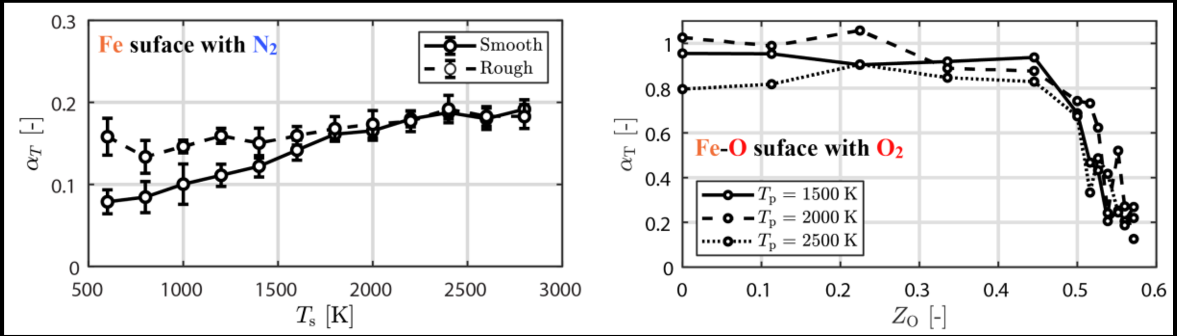
Determine TAC and MAC using MD simulations

Molecular beam simulations

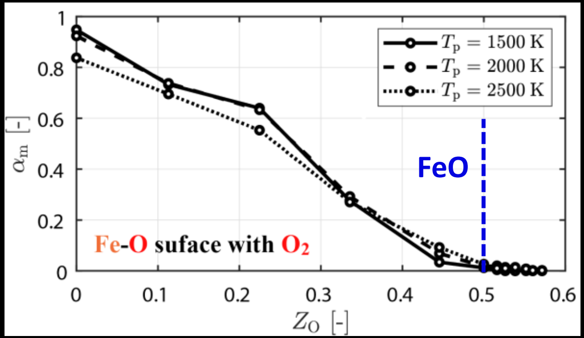


- Shoot a gas molecule towards a Fe-O mixture surface
- Repeat this simulation many times with different incident velocities according to the Maxwell-Boltzmann distribution
- Get ensemble-averaged results

Results of TAC



Results of MAC



Oxidation degree (or O molar fraction) of mixture:

$$Z_O = \frac{n_{O,s}}{n_{tot,s}}$$

Thijs, L.C., Kritikos, E., Giusti, A., Ramaekers, W.J., van Oijen, J.A., de Goey, L.P. and Mi, X.C., 2022. On the combustion of fine iron particles beyond FeO stoichiometry: Insights gained from molecular dynamics simulations. arXiv preprint arXiv:2212.06432.

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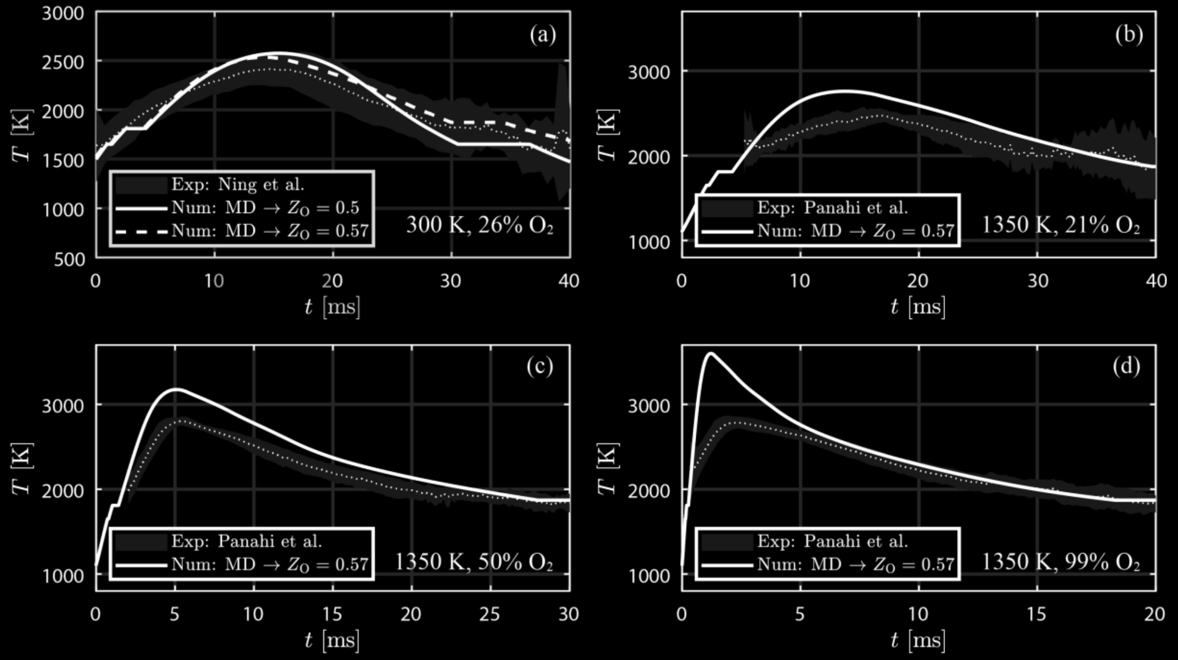
Results for single-Fe-particle combustion

Considering:
- Effect of heat/mass transfer in the Knudsen transition regime
- Surface chemisorption limit
- Oxidation beyond FeO

Assuming:
- Infinitely fast internal transport of Fe and O

Is internal transport the last missing piece of the puzzle?

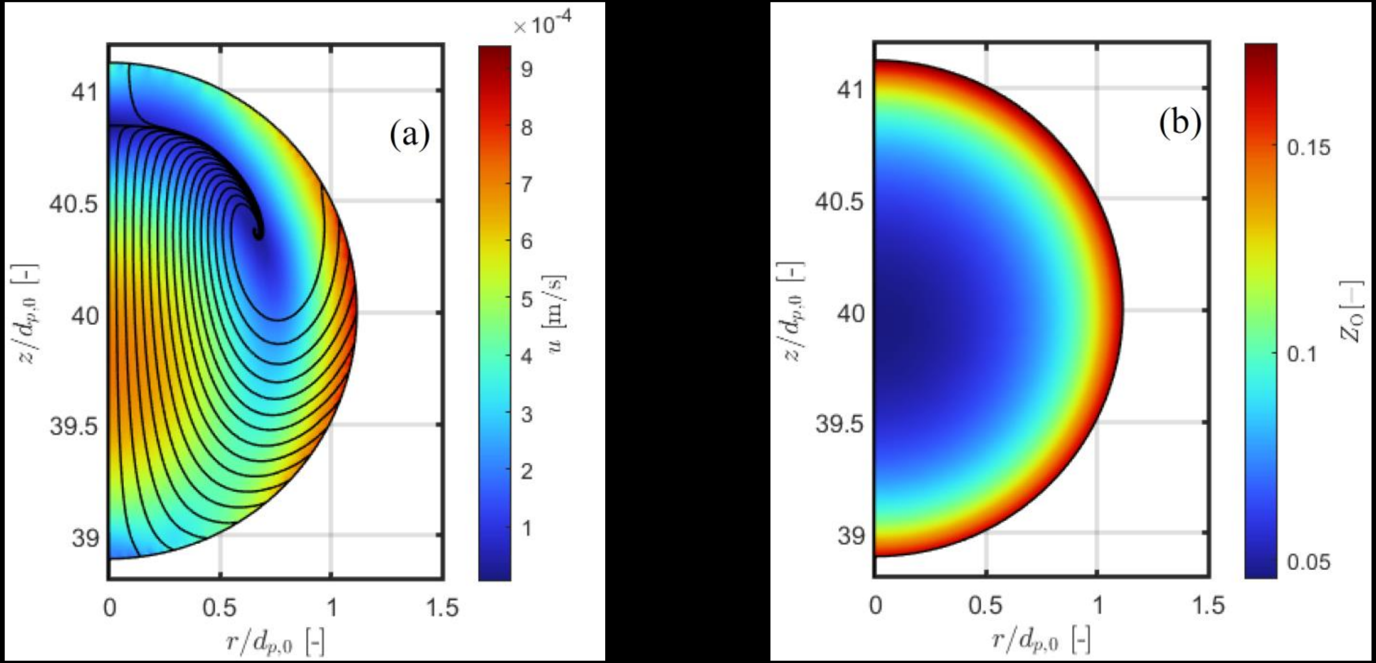


Thijs, L.C., Kritikos, E., Giusti, A., Ramaekers, W.J., van Oijen, J.A., de Goey, L.P. and Mi, X.C., 2022. On the combustion of fine iron particles beyond FeO stoichiometry: Insights gained from molecular dynamics simulations. arXiv preprint arXiv:2212.06432.

To consider a finite rate of internal transport

Particle-resolved model with MD-simulation-informed diffusion coefficients

Sample results for a 50-μm particle after 7 ms of constant oxidation:



Unpublished results obtained by Thijs et al. (2023)

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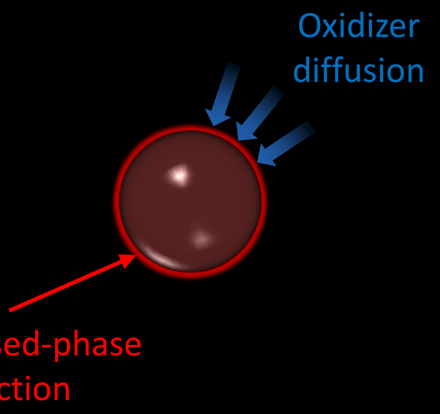
Unique features of iron-particle combustion

non-volatile combustion



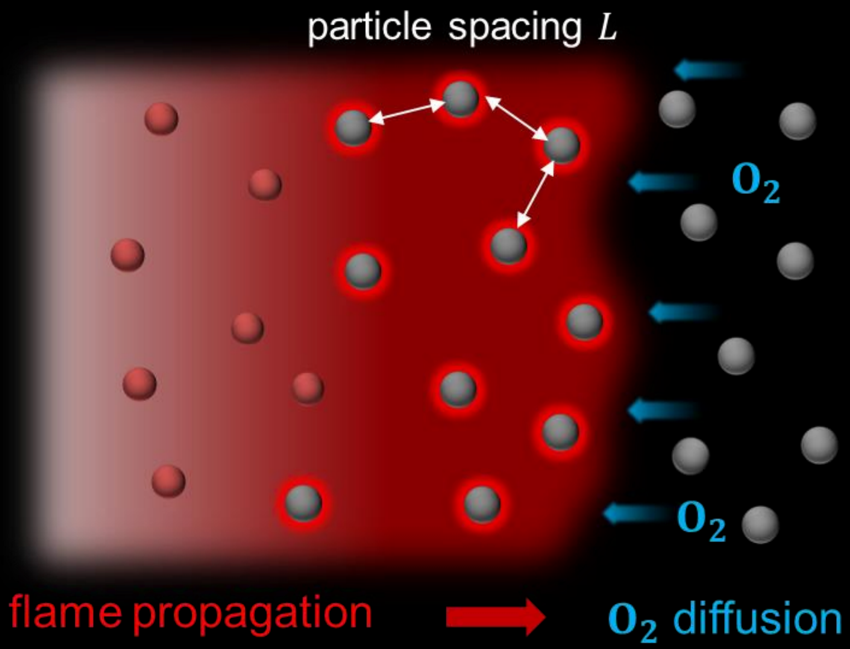
metals with ***high*** melting and boiling points,
e.g., ***iron***

Unique features

Heterogeneous oxidation processes

Spatially discrete flame propagation behavior

Unique flame dynamics: The discrete effect



$$\chi = \frac{t_{\text{reaction}}}{t_{\text{diffusion}}} = \frac{t_{\text{reaction}}}{L^2/\alpha}$$

α : Thermal diffusivity

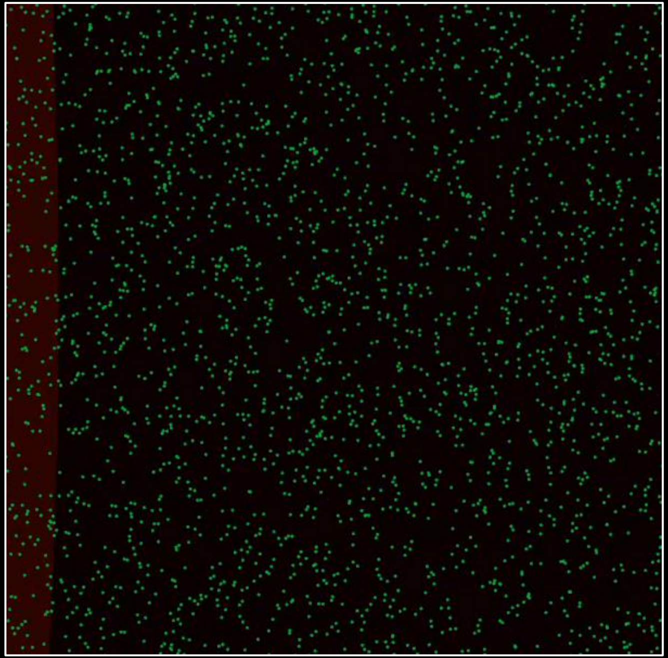
L : Average particle spacing

Goroshin, Lee, and Shoshin, *Proc. Combust. Inst*, 1998

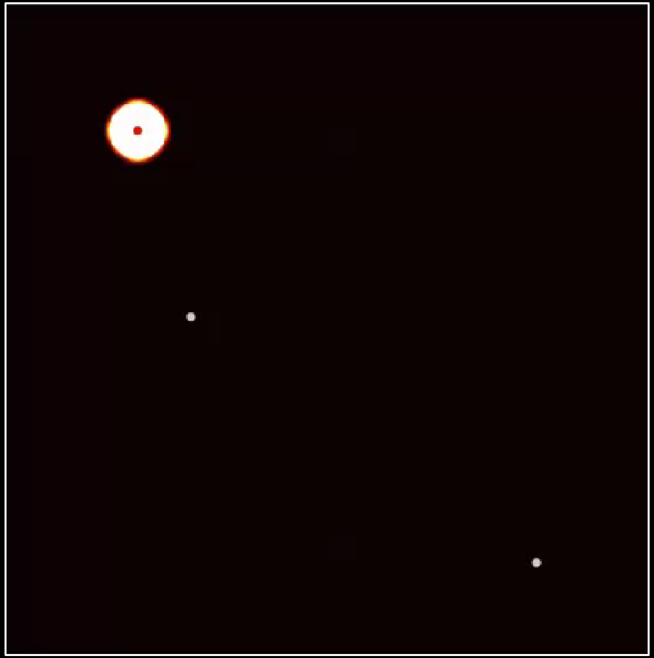
Reduced-order modeling illustration

$$\chi = \frac{t_{\text{reaction}}}{t_{\text{diffusion}}} = \frac{t_{\text{reaction}}}{L^2/\alpha}$$

α : Thermal diffusivity L : Average particle spacing



$\chi \gg 1$ Continuous



$\chi \ll 1$ Discrete

Lam, F., Mi, X. and Higgins, A.J., 2017. Front roughening of flames in discrete media. *Physical Review E*, 96(1), p.013107.

Unique features in turbulent flame of iron dust

A dimensional analysis assuming operational conditions similar to the Cambridge coal turbulent burner (Balusamy et al. 2013).

Length scales of the turbulence:

Inner tube diameter: $d_{\mathrm{in}} = 15.8\ \mathrm{mm}$
Mean injection speed: $\bar{U} = 9.16\ \mathrm{m/s}$

$\mathrm{Re} = 7500$

Integral length: $l \approx 0.5\text{-}1\ \mathrm{cm}$
Kolmogorov length: $l_{\mathrm{K}} \approx 100\ \mu\mathrm{m}$

Length scales of iron dust:

Particle size: $d_{\mathrm{p}} = 50\ \mu\mathrm{m}$
Mean particle spacing: $l_{\mathrm{p}} = 750\ \mu\mathrm{m}$
in air with equivalence ratio $\phi_{\mathrm{FeO}} = 1$

https://scitechdaily.com/irons-in-the-fire-smokeless-carbon-free-combustion/

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Multiscale interaction between reacting iron particles and turbulence:

- $d_{\mathrm{p}} < l_{\mathrm{K}}$ → Viscous drag dissipates turbulent kinetic energy (TKE).
- $l_{\mathrm{K}} < l_{\mathrm{p}} < l$ → Spatially discrete energy release produces TKE.
- Particle Stokes number can range from 0.01 to 10 → Particles are poorly entrained by the flow.

→ **Preferential concentration (or clustering) of particles**

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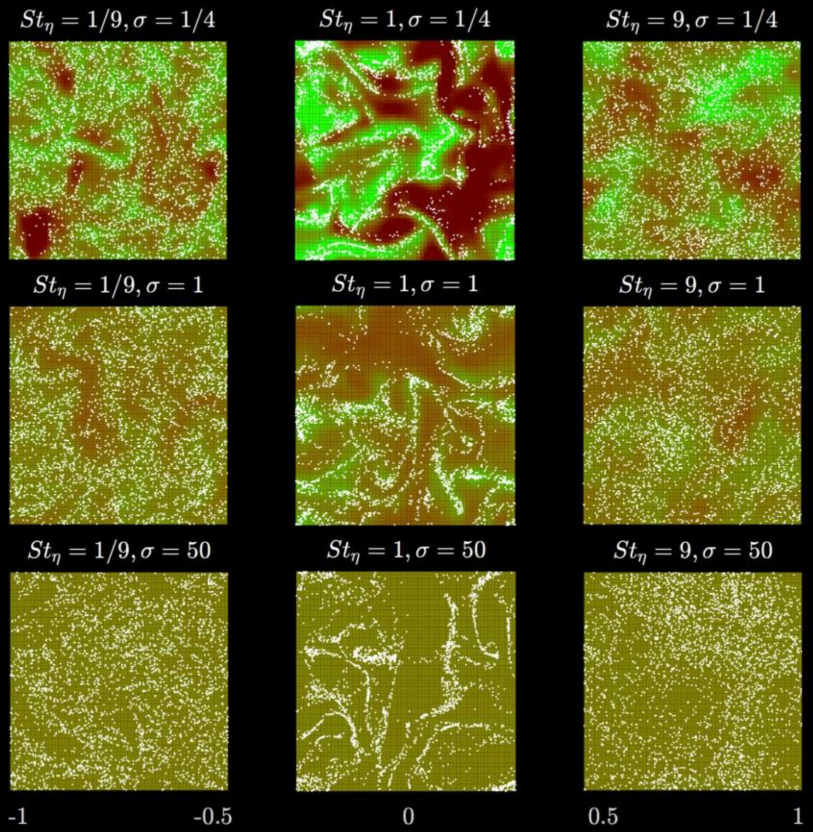
Preferential concentration around Kolmogorov $\mathrm{Stk} \approx 1$



Pouransari, H. and Mani, A., 2018. Particle-to-fluid heat transfer in particle-laden turbulence. Physical Review Fluids, 3(7), p.074304.

Why this is uniquely important in iron-dust combustion?

- Iron has a high density.

- Iron combustion is non-volatile, i.e., particles remain in condensed phases.

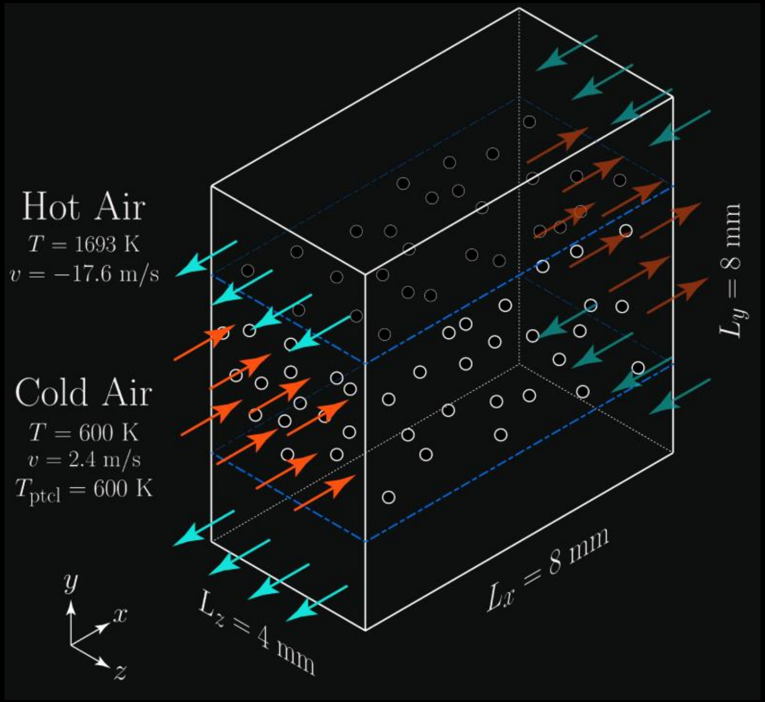
Effects on iron-dust combustion:

- Significantly changes local particle number density → Particle collision and agglomeration.

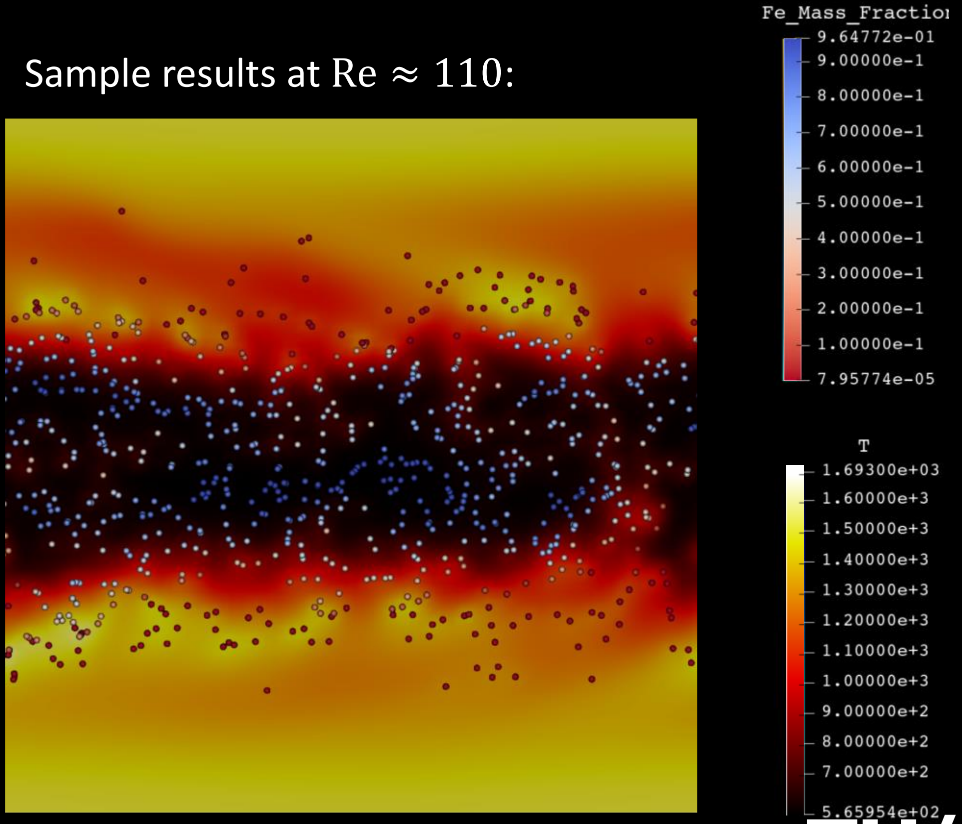
- Significantly changes local equivalence ratio → local quenching at a lower oxidation degree

Preliminary efforts to study iron-dust combustion in turbulence

Mixing layer simulations:



Sample results at Re ≈ 110:



Unpublished results obtained by Hemamalini et al. (2023)

TU/e

Outstanding problems

- To determine ignition conditions of single and dispersed cloud of iron particles
- Heat release rate (HRR) of iron particles at different oxidation stages:
    - Heterogeneous oxidation mechanisms
    - Spatially non-uniform combustion in turbulence
    - Radiative heat transfer among the particles and to the surrounding
- Understand and reduce emissions of NOx and oxide nanoparticles

Thank you! Questions?

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