Direct reduction of chromite for ferrochrome production (DRC)

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Chromite/Ferrochrome Project

- Ring of Fire (RoF) chromite deposits considered world-class and as such offer a significant potential for economic development and technological innovations
- In alignment with Government of Canada's commitment
  - responsible development of the RoF resources to maximize Canadian value and benefits from the deposits
- Project aims to develop new energy efficient and clean technologies with the following outcomes:
  - Companies equipped with technological capacity to bring their deposits to production with reduced CAPEX/OPEX
  - Canada is competitive as a new market entrant in chromite/ ferrochrome production
- C$8.3 M funding over 6 years (2015-20)

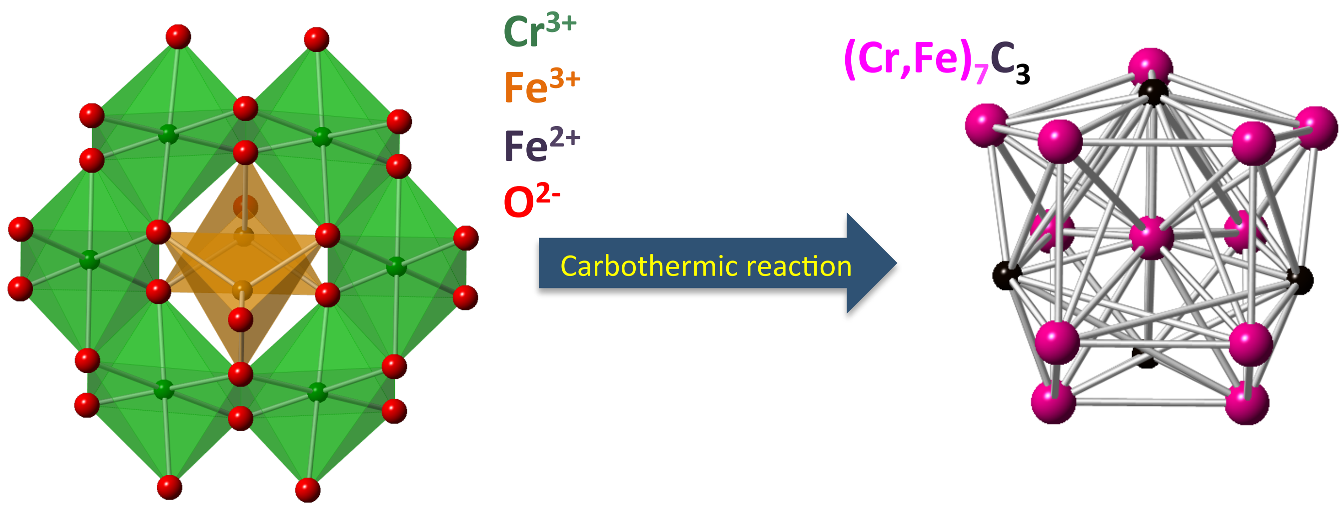
Chromite/Ferrochrome Project

- Focussed on innovation - generation of new knowledge
  - developing a fundamental-level understanding of carbothermic reactions and evolution of Cr and Fe species during reduction
  - identification of clean and technologically most advanced flow sheets
  - designing flow sheet of "made-in Canada" ferrochrome facility
- Addresses environmental impacts and health concerns
  - Cr^{6+} generation during processing
  - slag reutilization
  - minimizing carbon and mining footprints
- Aims for improved resource utilization
  - processing of lower grade ores
  - recovery of chromite fines

Ferrochrome production

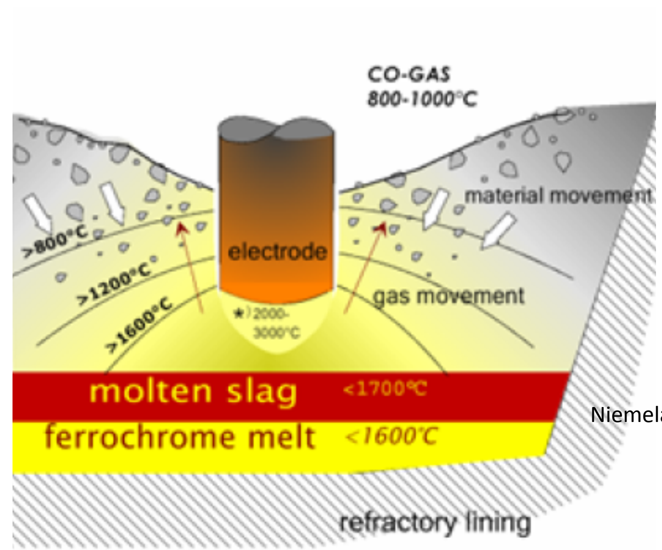
$(Mg_{0.4}Fe_{0.6})(Al_{0.6}Fe_{0.1}Cr_{1.3})O_4 + 3.66C \rightarrow 0.28Cr_{4.6}Fe_{2.4}C_3 + 0.3MgAl_{1.6}Mg_{0.4}O_4 + 2.8CO$

chromite (RoF) *ferrochrome (RoF)*



total energy needed to break M-O bonds >> total energy of Fe-Cr-C bonds
Enthalpy of reaction (ΔH) is high (highly endothermic)

Ferrochrome smelting in submerged electric arc furnaces



Niemela & Kauppi (2007)

- Smelting processes energy intensive
- Energy requirements can exceed 4 MWh/t [1]
- GHG emissions can exceed 1 t CO_2 /t FeCr produced
- SEC reduced by about one third through pre-reduction (Premus)[2]

[1] Naiker & Riley 2006; Beukes et al. 2015
[2] Naiker 2007

Need for new alternate technologies

- Thermodynamic simulations and exploratory experimental work
  - Carbothermic reduction of chromite using various fluxes (800-1400 °C)
  - In-situ reduction and metallization occurring on carbon particles
  - Presence of molten media during reactions
  - Conceptualized segregation reduction mechanism
  - Screened fluxes (melting point <1300 °C > boiling point; low viscosity liquid slag

Process/engineering opportunity

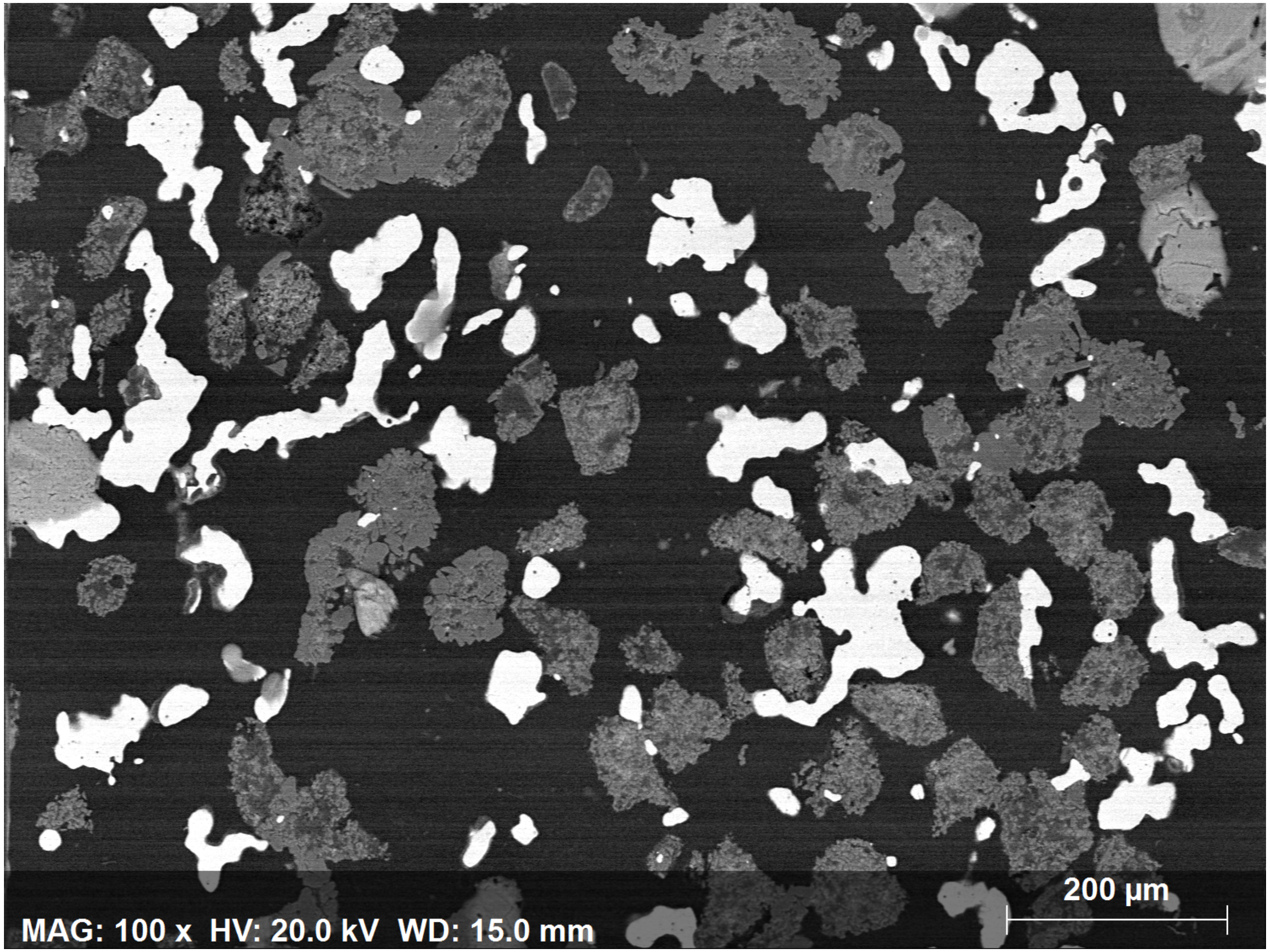
- Critical evaluation and testing of KWG patent (alkali-assisted reduction)
- Experimental studies using selected fluxes (alkalis, chlorides, fluorides, borates, SPL)
  - Objectives: high Cr metallization, fast kinetics, alloy growth, fundamental understanding
  - Experimental design parameters
    - Ore composition and particle size
    - Reductant type and particle size
    - Flux concentration; temperature; reduction kinetics
    - Feed form (i.e. pellets vs. loose)
- Advanced characterization studies
  - Synchrotron-based EXAFS, XANES, time-resolved HE-XRD

Advanced Photon Source Synchrotron Facility

Direct reduction (DRC) at 1300 ˚C for 1-2h

- NaOH flux
  - Ore:Reductant:Flux 100:22:12 (by weight)
  - 85% Cr metallization; $Cr_{4.7}Fe_{2.3}C_3$
- $CaCl_2$ flux
  - Ore:Reductant:Flux 100:19:30 (by weight)
  - >94% Cr metallization; $Cr_{4.7}Fe_{2.3}C_3$
- Metallurgical waste product:
  - Ore:Reductant:Flux 100:23:30 (by weight)
  - >93% Cr metallization

$CaCl_2$-assisted direct reduction (DRC)

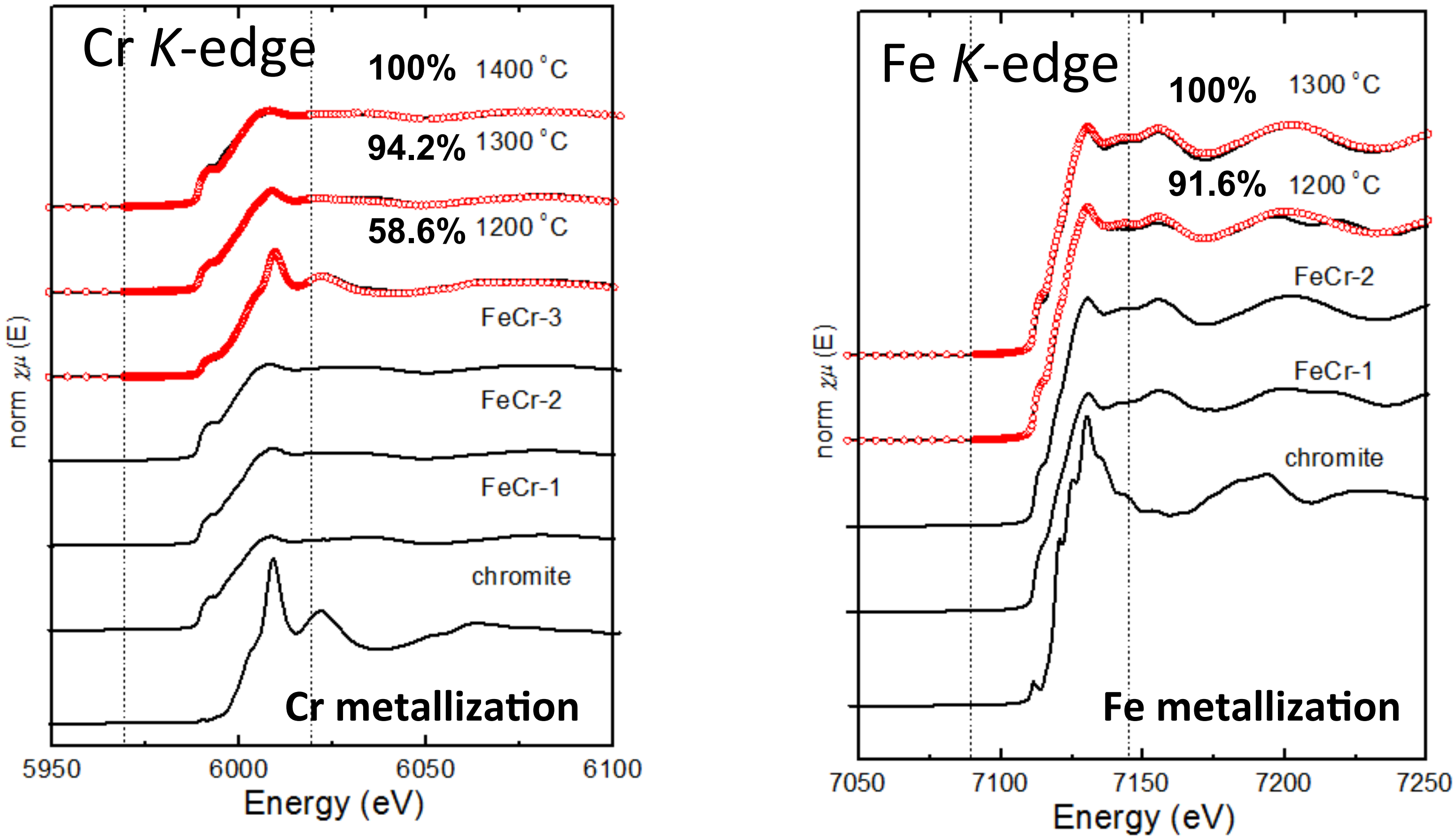


Ore:Carbon:Flux 100:19:30; 1300 ˚C at 2h

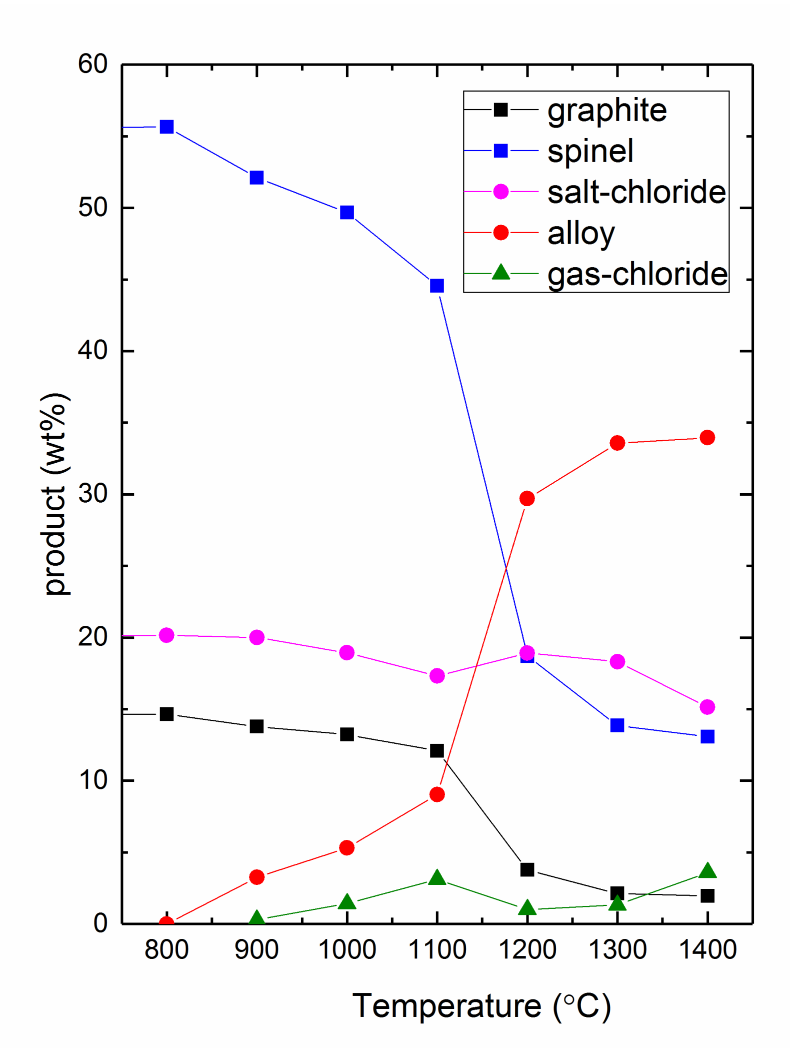
Degree of metallization: 98 % Cr & 100 % Fe

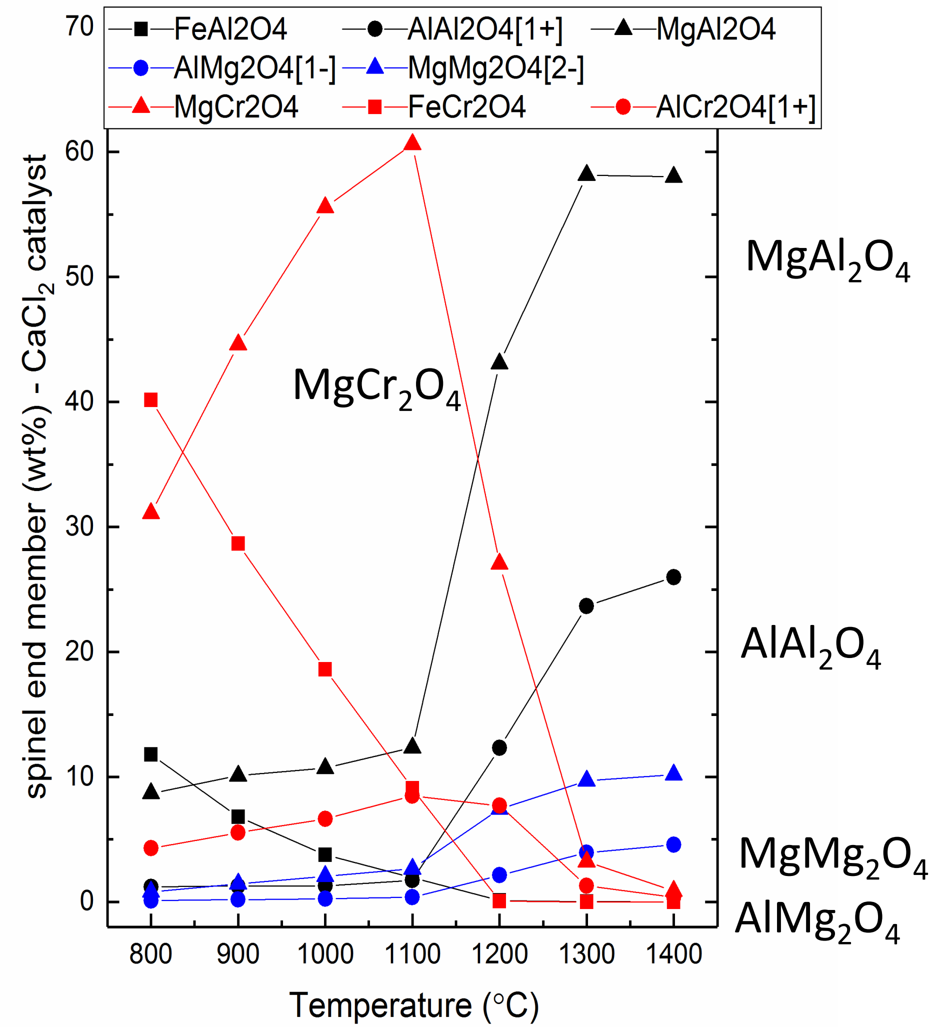
Degrees of metallization with $CaCl_2$

Synchrotron X-ray Absorption Spectroscopy (XANES)



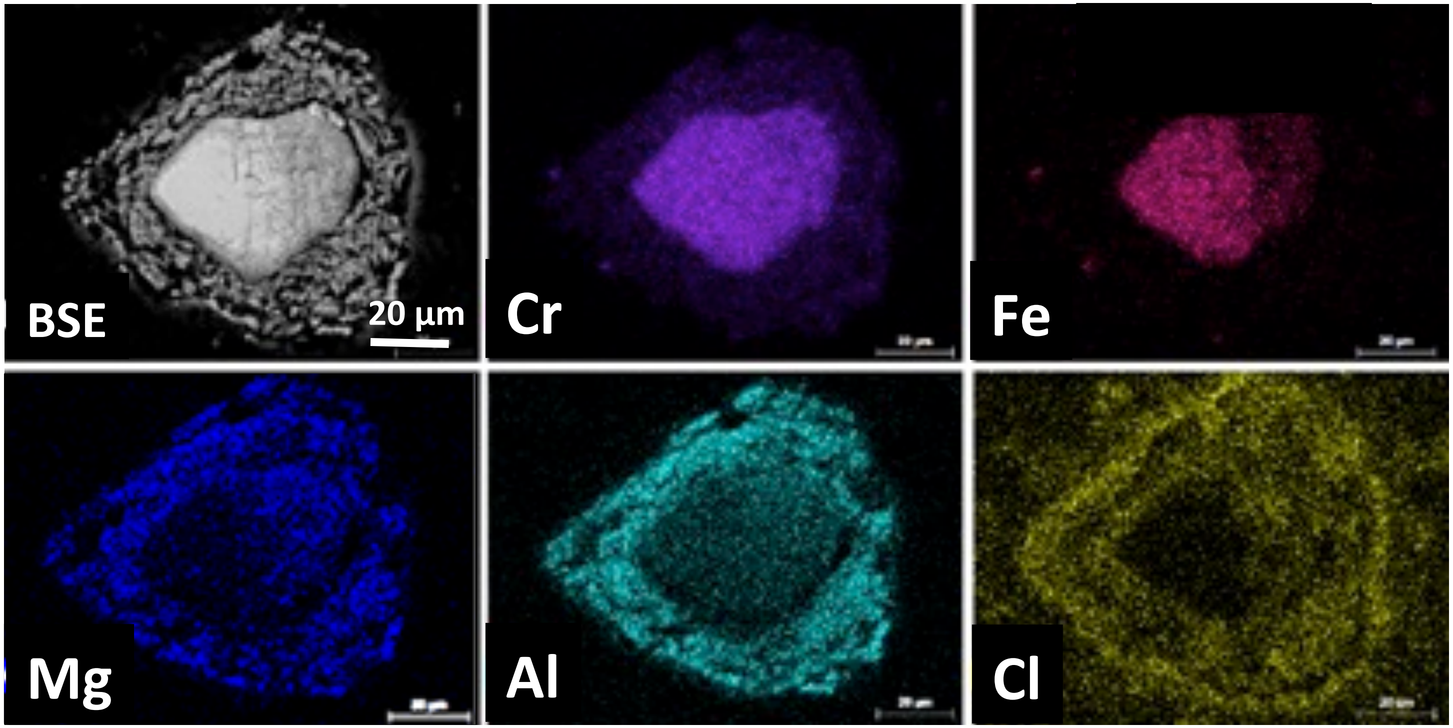
Thermodynamics of $CaCl_2$-assisted DRC

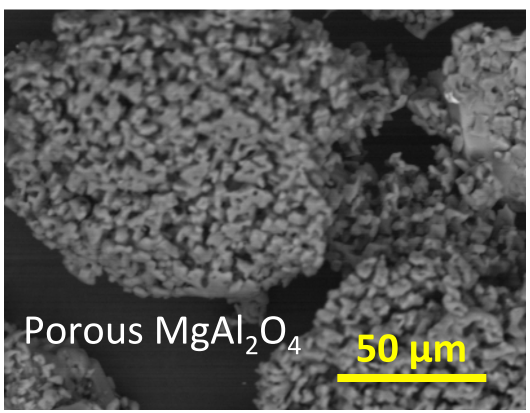


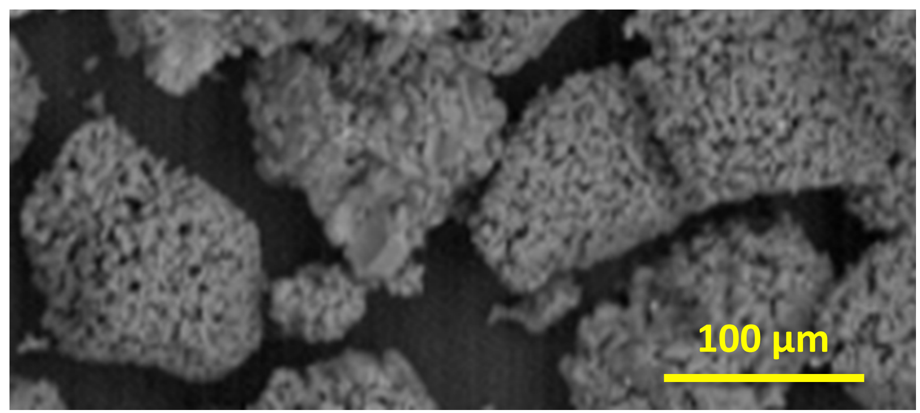


Ore:Carbon:Flux 100:22:30; chromite:84%, clinochlore 16%

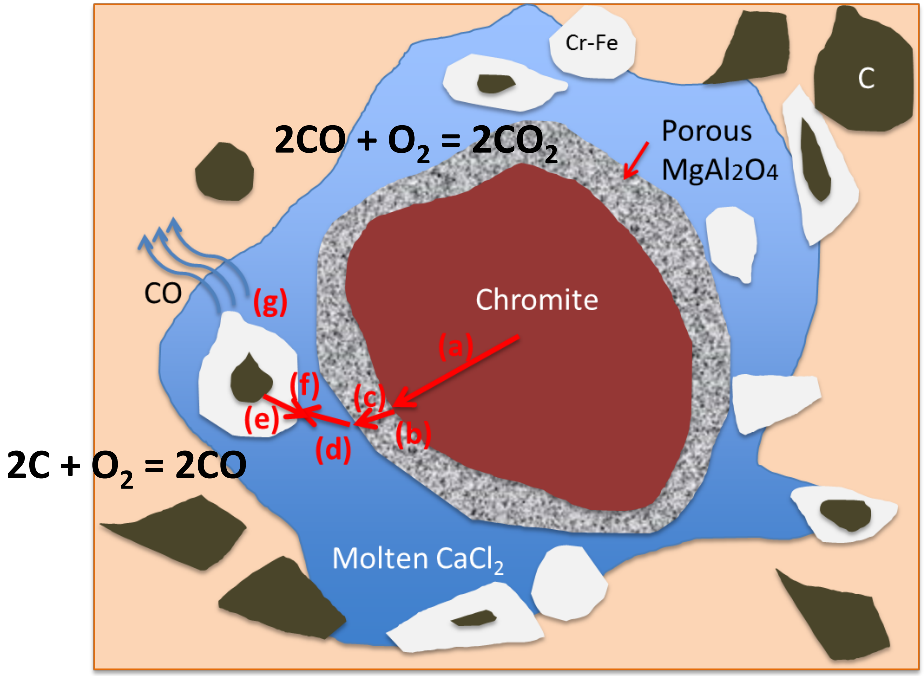
Dissolution of chromite during $CaCl_2$-assisted DRC







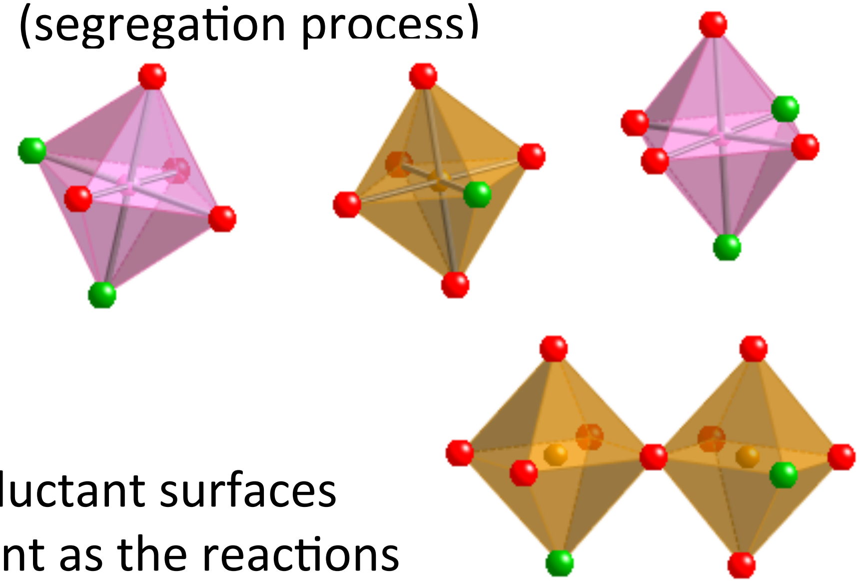
Mechanism of $CaCl_2$-assisted DRC



- Incongruent dissolution of chromite in molten $CaCl_2$

  $Cr_2O_3(\ell)$ + $FeO(\ell)$ + $MgAl_2O_4(s)$

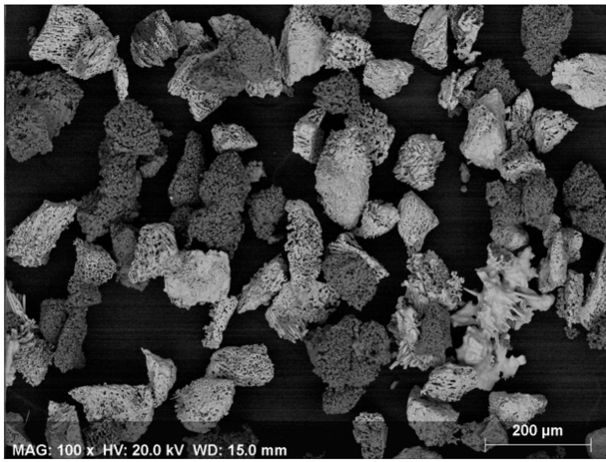
- Transport of Cr^{3+} and Fe^{2+} as ionic species (O^{2-}, Cl^-) in liquid & gas phase (segregation process)



- Reduction and metallization on solid reductant surfaces
- Shrinking cores of chromite and reductant as the reactions proceed

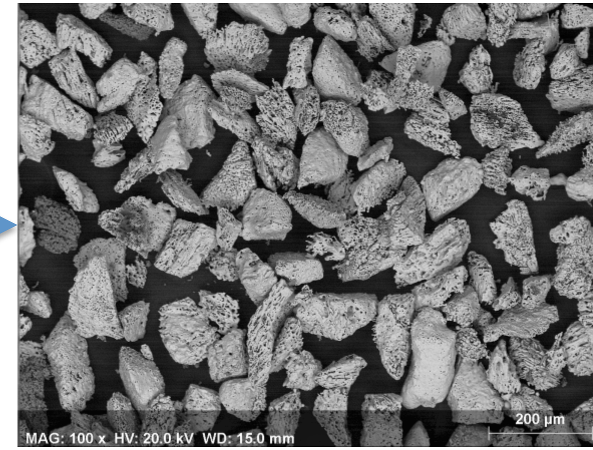
Liberation and recovery of FeCr ($CaCl_2$–assisted DRC)

Furnace product at 1300˚C after 2h

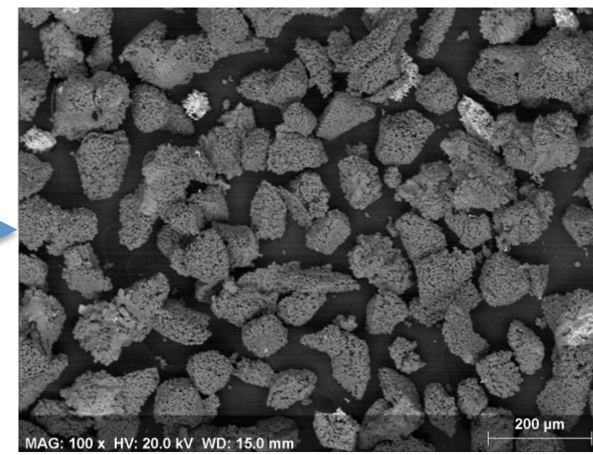


Light grey: FeCr
Dark grey: slag/gangue

magnetic fraction

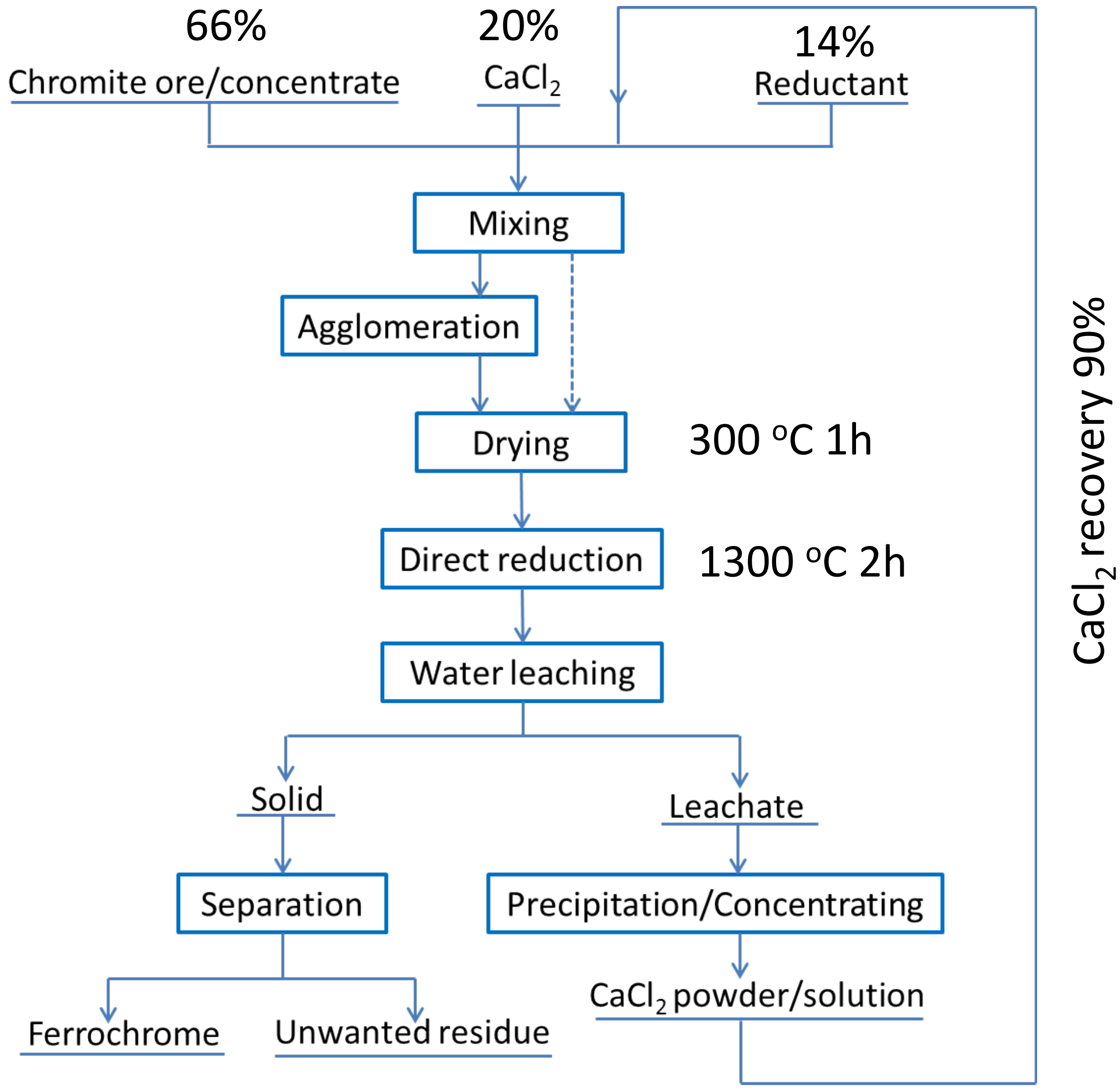


non-magnetic fraction



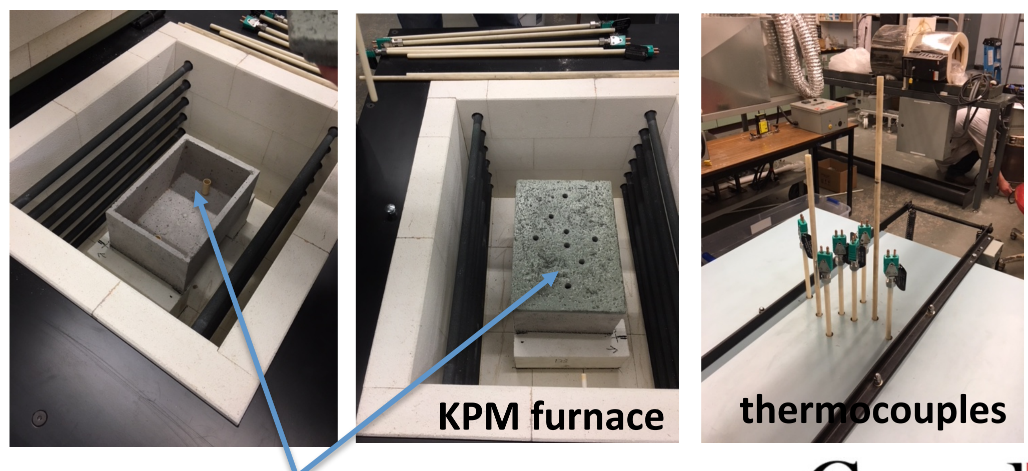
Metal recoveries through elutriating tube: 83.5% Cr & 90.6% Fe (not optimized)

Process Flow Diagram ($CaCl_2$-assisted DRC)



Towards commercialization of DRC technology

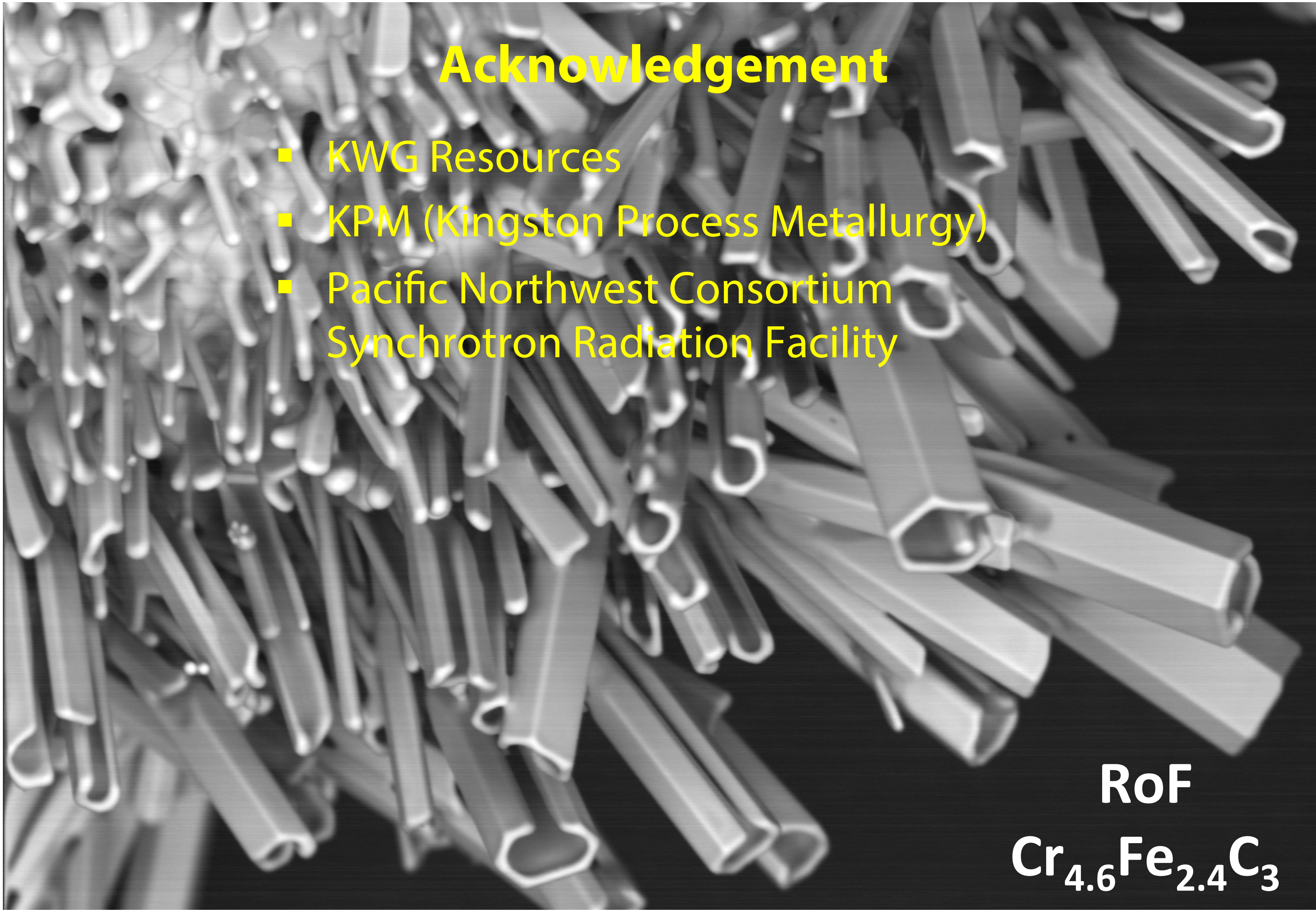
- Review of furnace technologies for their potential adaption to DRC
  - Direct reduced iron technologies
    - Shaft (MIDREX), RK, RHF (FASTMET, Shenwu), Fluidized-bed reactors
    - natural gas, coal based
  - Pre-reduction/treatment of chromite (SRC, Premus)
- CFD modelling of select potential reactors (RK, RHF)
  - Heat transfer, reactive mass transport, residence time, throughput capacity, material flow, residence time, thermodynamics
  - Implications in terms of carbothermic reactions and degree of metallization
- Scaling-up
  - Batch reactor (~2 kg)
    - Heat transfer limitations
    - Oxygen ingress and flow



SiC-Al_2O_3-SiO_2 crucible: 29x20x13 cm

Summary of findings

- DRC at 1300 ˚C
  - High degrees of Cr metallization with NaOH, $CaCl_2$ and a metallurgical waste
  - Reduction rates are 3 times and greater than the rate with no-flux
  - Alloy particle growth controlled by reductant particle size and porosity
- FeCr production through flux-assisted DRC is possible
  - Segregation process minimizes the formation of fine alloy particles within chromite and enables liberation and subsequent physical separation
- Commercialization of DRC technology is promising
  - Two potential furnace technologies identified (RK and RHF)
  - Several challenges remain; however, operational experience with Premus RK is positive
  - Worst-case scenario would be utilization as a “pre-reduction” process with potential for significant reductions in SEC (i.e. >1.6 MWh/t FeCr)
  - **Potential economic benefits would justify technology development**



Acknowledgement

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