Direct reduction of chromite for ferrochrome production (DRC)

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ICDA 2018, April 25, 2018, Paris
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

\[(\text{Mg}_{0.4}\text{Fe}_{0.6})(\text{Al}_{0.6}\text{Fe}_{0.1}\text{Cr}_{1.3})\text{O}_4 + 3.66\text{C} \rightarrow 0.28\text{Cr}_{4.6}\text{Fe}_{2.4}\text{C}_3 + 0.3\text{MgAl}_{1.6}\text{Mg}_{0.4}\text{O}_4 + 2.8\text{CO}\]

*chromite (RoF)*

*ferrochrome (RoF)*

Enthalpy of reaction (\(\Delta H\)) is high (highly endothermic)
Ferrochrome smelting in submerged electric arc furnaces

- 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)

- 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%, clinohlochlore 16%
Dissolution of chromite during CaCl$_2$-assisted DRC
Mechanism of CaCl$_2$-assisted DRC

- Incongruent dissolution of chromite in molten CaCl$_2$
  \[ \text{Cr}_2\text{O}_3(\ell) + \text{FeO}(\ell) + \text{MgAl}_2\text{O}_4(\text{s}) \]
- 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

Metal recoveries through elutriating tube: 83.5% Cr & 90.6% Fe (not optimized)
Process Flow Diagram (CaCl$_2$-assisted DRC)

66% Chromite ore/concentrate

20% CaCl$_2$

14% Reductant

Mixing

Agglomeration

Drying

300 °C 1h

Direct reduction

1300 °C 2h

Water leaching

Solid

Leachate

Separation

Precipitation/Concentrating

CaCl$_2$ powder/solution

Ferrochrome

Unwanted residue

CaCl$_2$ recovery 90%
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$_2$O$_3$-SiO$_2$ crucible: 29x20x13 cm

KPM furnace

thermocouples
Summary of findings

- **DRC at 1300 °C**
  - High degrees of Cr metallization with NaOH, CaCl₂ 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

- KWG Resources
- KPM (Kingston Process Metallurgy)
- Pacific Northwest Consortium Synchrotron Radiation Facility

\[
\text{RoF} \\
\text{Cr}_{4.6}\text{Fe}_{2.4}\text{C}_3
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