Development of beneficiation processes for low-grade manganese ores for the ferroalloy industry

By D.A. Barrett

Co-authors: Prof. Margreth Tadie (SU), Prof. Bjorn von der Heyden (SU), and Dr. Robert Cromarty (UP)

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Introduction

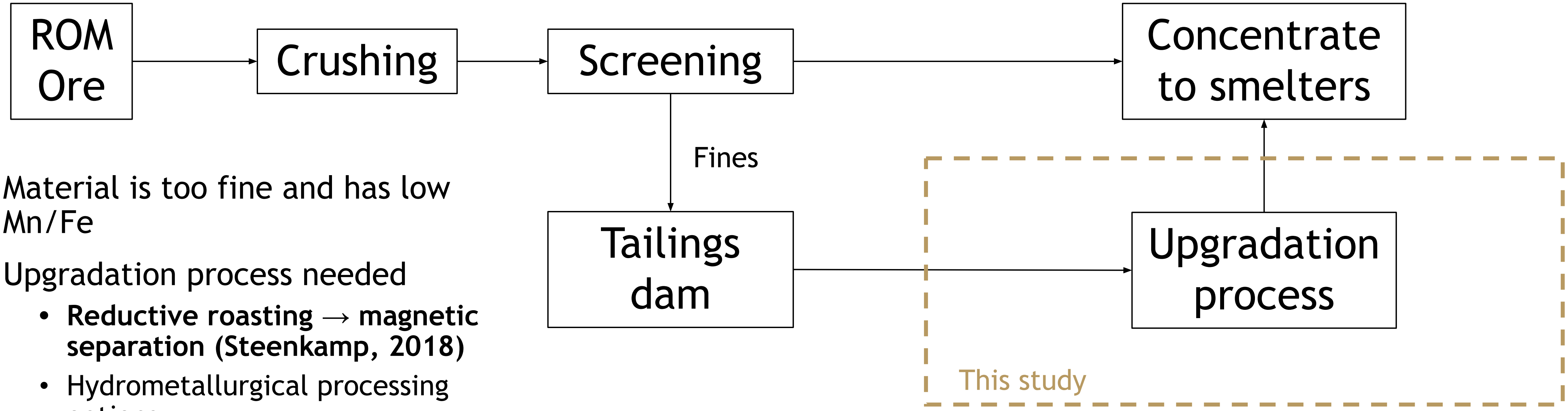
- Manganese (Mn) has global economic importance
- Used in the ferroalloy industry
  - **Smelter feed requires 44% Mn and Mn/Fe >7.5**
- Kalahari Manganese Field
  - Largest land-based Mn deposit
  - 70% resources & 38% reserves globally

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Simplified Flowsheet



- Material is too fine and has low Mn/Fe
- Upgradation process needed
  - **Reductive roasting → magnetic separation (Steenkamp, 2018)**
  - Hydrometallurgical processing options

Stellenbosch University Iyunivesithi Universiteit
African Rainbow Minerals Chair in GeoMetallurgy
ARM African Rainbow Minerals

Ties to geometallurgy

- Orebody is highly variable
  - Wide range of Fe content in Mn minerals and Mn content in hematite
  - Geometallurgical models → know what Mn and Fe levels to expect
- Minerals can have unique reduction characteristics
- Statistical modelling useful in predicting behaviour
- Flowsheet design
  - Improve full orebody utilization
  - Reduce carbon emissions

Process selection

- Process can be selectively applied based on geometallurgical domains
  - High Mn/Fe ores → standard beneficiation
  - Low Mn/Fe ores → upgradation required
- Mineralogy can guide operating parameters
- Plan ore blending based on expected output

The problem

- Processing fines from Nchwaning mine
  - Particle size too fine → make briquettes
- Fines contain 44% Mn and Mn/Fe = 2.6
  - Mn grade is acceptable
  - Mn/Fe <<< 7.5
  - Iron needs to be separated from starting material

Iron deportment

- Hematite
- Bixbyite
- Braunite I/II

Manganese deportment

- Braunite I/II
- Bixbyite
- Manganite

XRD - untreated ore

Mineral name	Formula	Mass %
Braunite	$Mn^{2+}Mn^{3+}_6(SiO_4)O_8$	61.0
Hematite	Fe_2O_3	23.2
Manganite	$Mn^{3+}O(OH)$	7.9
Calcite	$CaCO_3$	6.1
Rhodochrosite	$MnCO_3$	0.7
Birnessite	$(Na, Ca)_{0.5}(Mn^{4+}, Mn^{3+})_2O_4 \cdot 1.5H_2O$	0.7
Magnussonite	$Mn^{2+}_{10}(As^{3+}O_3)_6(OH, Cl)_2$	0.03

Stellenbosch University Iyunivesithi Universiteit | African Rainbow Minerals Chair in GeoMetallurgy | ARM African Rainbow Minerals

Carbothermic pre-reductive roasting

- The most researched and developed (Larssen et al, 2020)
  - Mn oxides → MnO & Fe oxides → FeO
  - 600 – 800 °C to limit Boudouard reaction → $C + CO_2\ (g) \rightarrow 2CO\ (g)$
  - CO/CO_2 atmosphere
- Leads to formation of (Mn, Fe)O for ferruginous material (Matabadal, 2022)
  - Difficult to separate
  - Higher temperatures / different reductant required to form metallic Fe
- Large environmental footprint
  - FeMn = 6.1 million tons CO_2 per annum
  - SiMn = 17.5 million tons CO_2 per annum

PARIS2015 UN CLIMATE CHANGE CONFERENCE COP21·CMP11

Approach

- Different atmosphere (Ernst et al., 2024)
  - H_2/H_2O
  - Pure H_2
- H_2 mixtures = increased extent and rate of reduction
- Pure H_2 more so as well as producing metallic Fe
  - Can be separated magnetically (Kivinen et al., 2010)
- Does not add carbon to the process

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

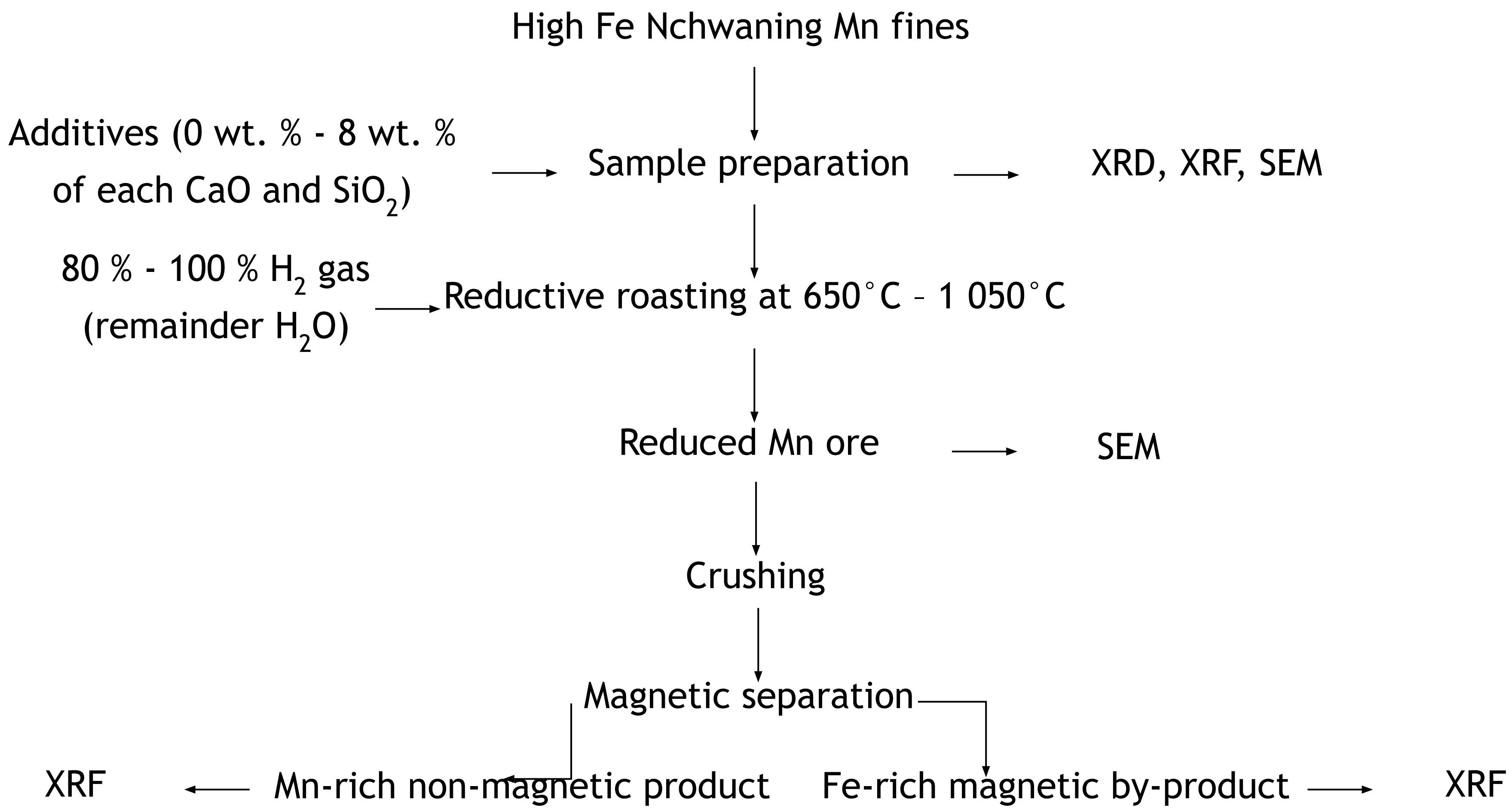
ARM African Rainbow Minerals

Objectives

- Develop a beneficiation process for low-grade Mn tailings → hydrogen-rich reductive roasting followed by magnetic separation
  - Produce suitable feed for ferroalloy production
- Investigate optimal working conditions for the chosen process
  - Mn/Fe ratio
  - Mn grade
  - Mn recovery
- Investigate the influence of mineralogical variability on the process

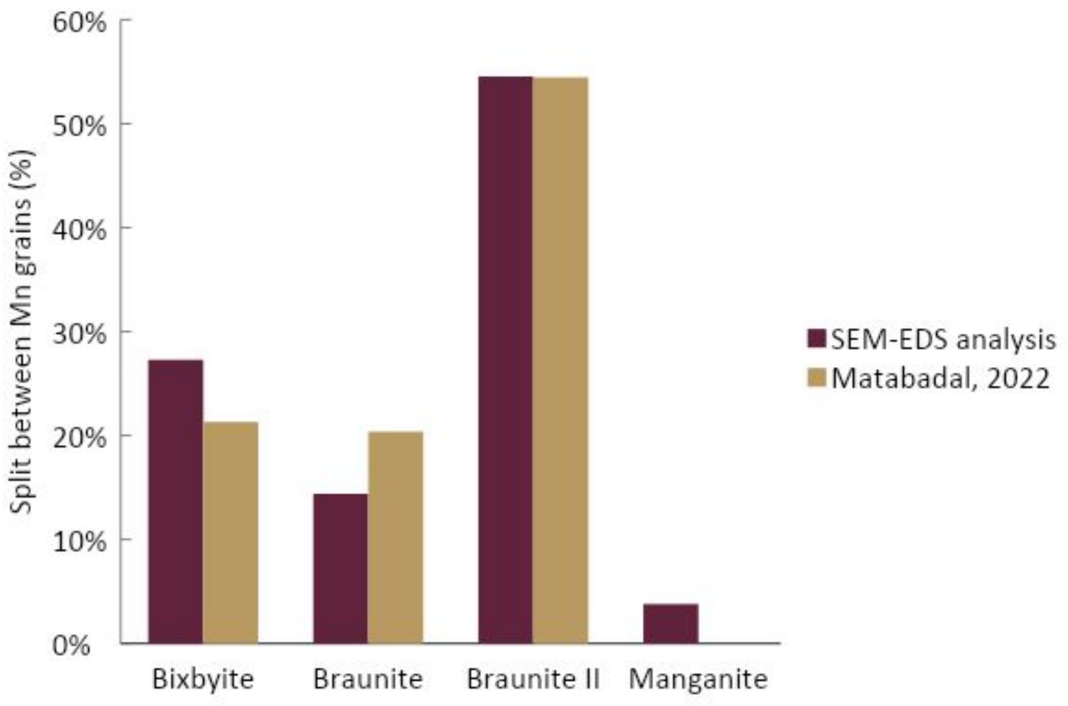
Stellenbosch University Iyunivesithi Universiteit
African Rainbow Minerals Chair in GeoMetallurgy
ARM African Rainbow Minerals

Methodology



SEM-EDS bulk analysis – Mn minerals

- XRD not able to split between bixbyite, braunite and braunite II
- Applied cation balance and decision tree between major minerals using SEM-EDS data
- Agrees with XRD analysis done on the same fines dump



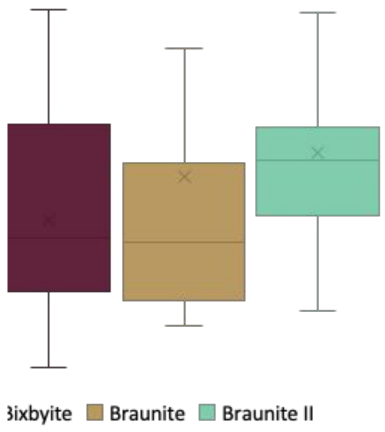
Stellenbosch University Iyunivesithi Universiteit

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

SEM-EDS bulk analysis - Fe content in Mn minerals

- Braunite II is the most abundant and contains the most Fe
- Bixbyite has wide range due to substitution series
- Braunite has the lowest median but a high average due to outliers



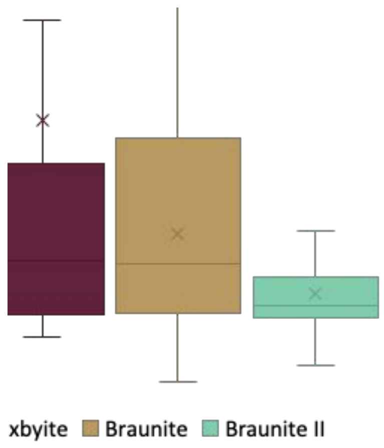
Stellenbosch University Iyunivesithi Universiteit

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

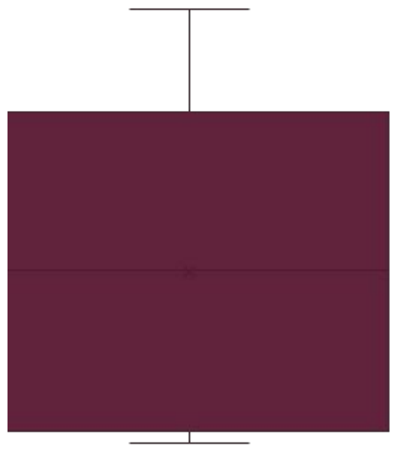
SEM-EDS bulk analysis – Mn/Fe in Mn minerals

- Bixbyite has highest mean Mn/Fe ratio due to a few grains with no Fe
- Braunite II has the lowest as expected
- Braunite with the widest range



SEM-EDS bulk analysis – Hematite

- 44% of grains analyzed contain < 2 mass % Mn
- Higher levels of Mn will influence activity and reducibility

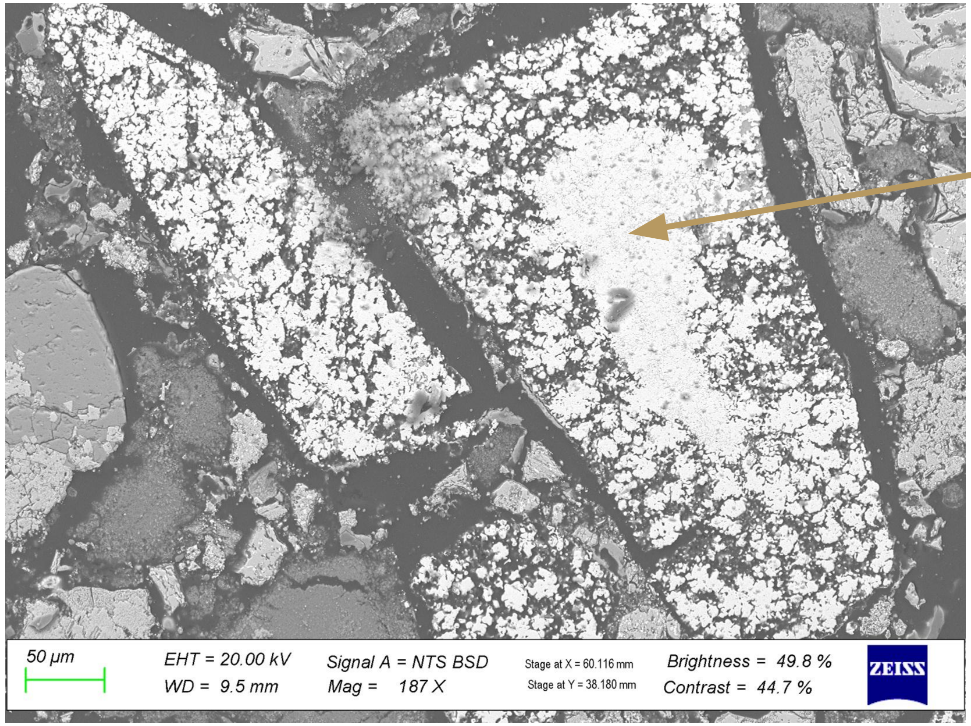


Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

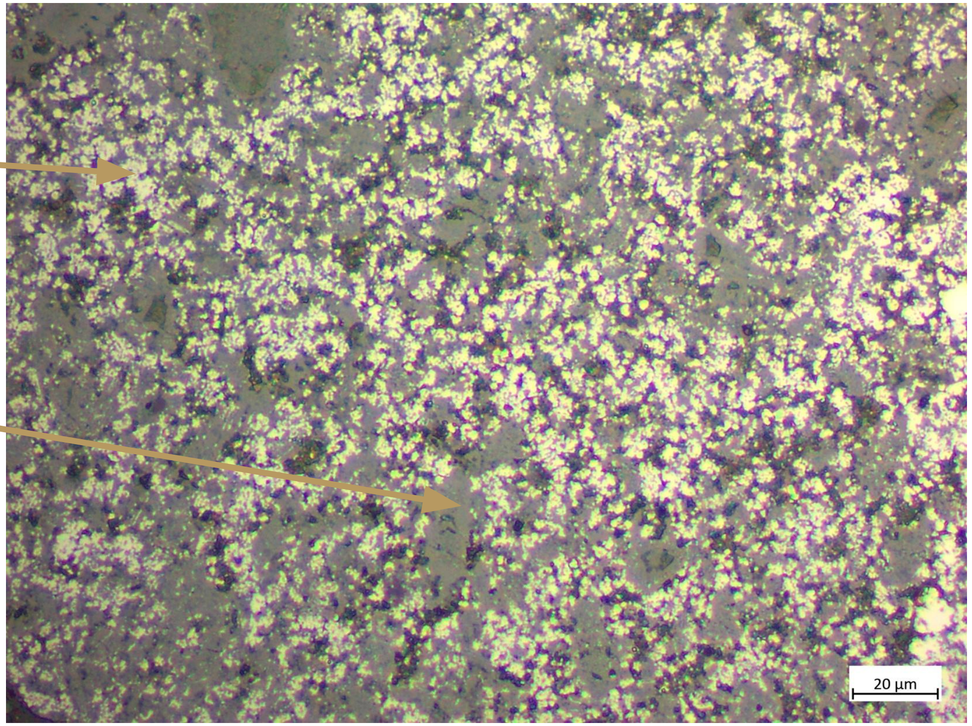
ARM African Rainbow Minerals

Influence of impurities in hematite reduction



Metallic Fe

Mn oxide



- Fully reduced metallic Fe
- Partially reduced treated hematite with Mn impurities

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

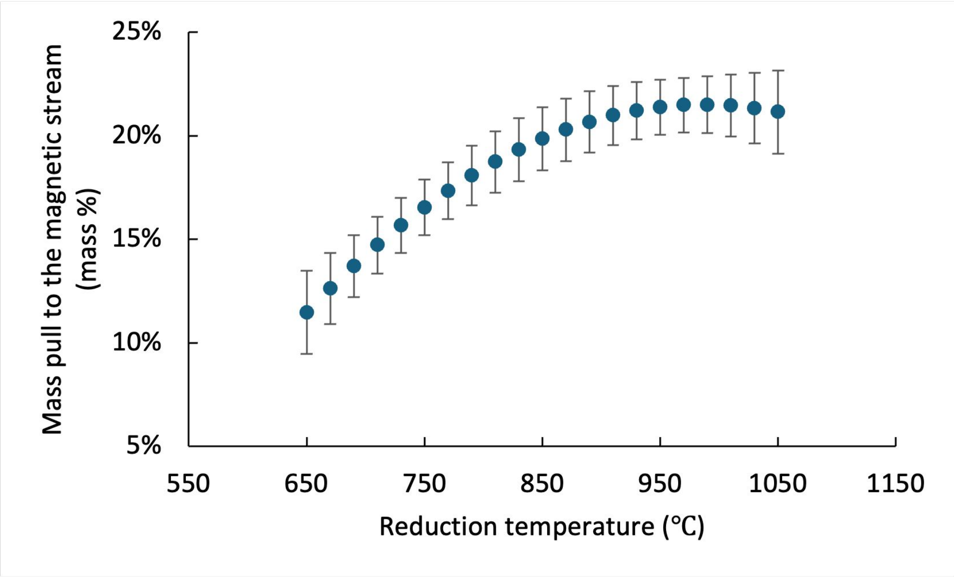
African Rainbow Minerals Chair in GeoMetallurgy

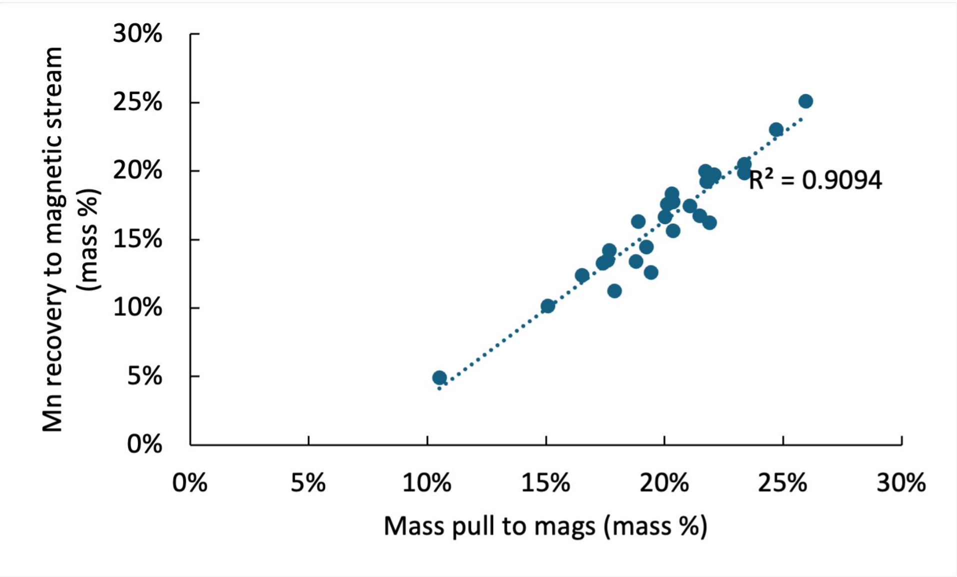
ARM African Rainbow Minerals

Experimental results

- Mn grade between 50% - 63% ✅
- Mn recovery 73% - 91% ✅
- Mn/Fe ratio 3.43 – 4.52
  - Poor separation between Mn and Fe
  - Why?

Desirability curves- mass pull / Mn recovery





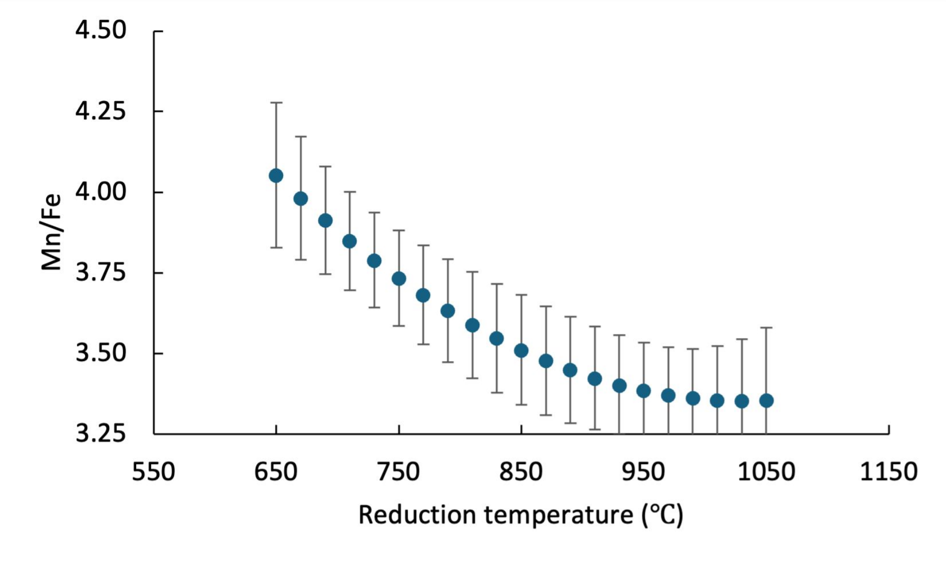
- Levels out due to reduction nearing completion
- Mn associated particles reporting to magnetic stream

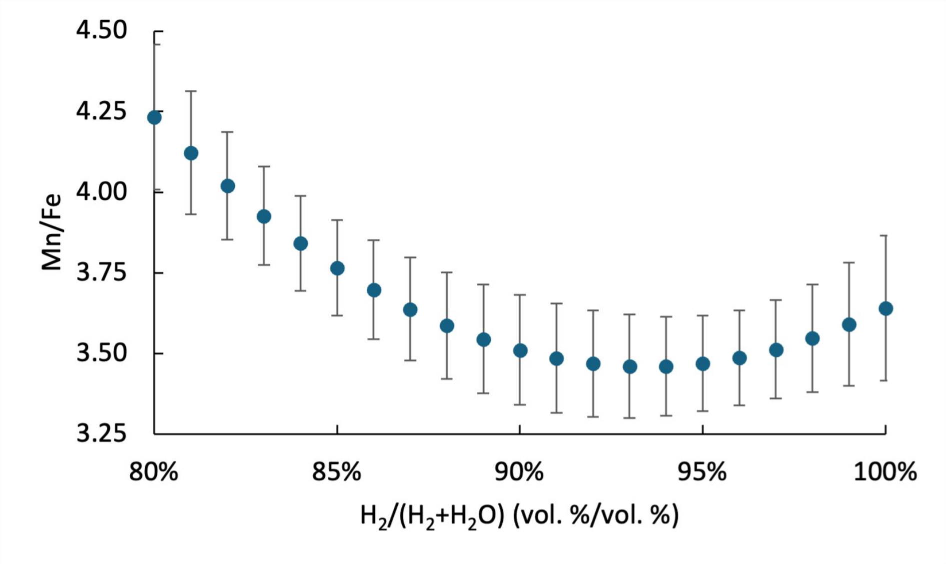
Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Desirability curves- Mn/Fe





- Less influence as reduction nears completion

- Uptick at end due to T centre point

Comparison between runs

- Theoretical maximum Mn/Fe achievable = all metallic Fe that forms gets removed perfectly and only oxide is left
- Run 1 had the best overall performance

Run	Mn/Fe oxide	Mn/Fe after separation	Percent achieved
1	**5.47**	**4.52**	**82.5%**
5	5.11	4.22	82.6%
16	20.20	3.58	17.7%
24	9.42	3.55	37.7%
25(C)	10.23	3.53	34.6%

Runs 1 and 5: Mildly reducing (750 °C & 85% H_2)

Run 16: New phase forming (950 °C & 95% H_2)

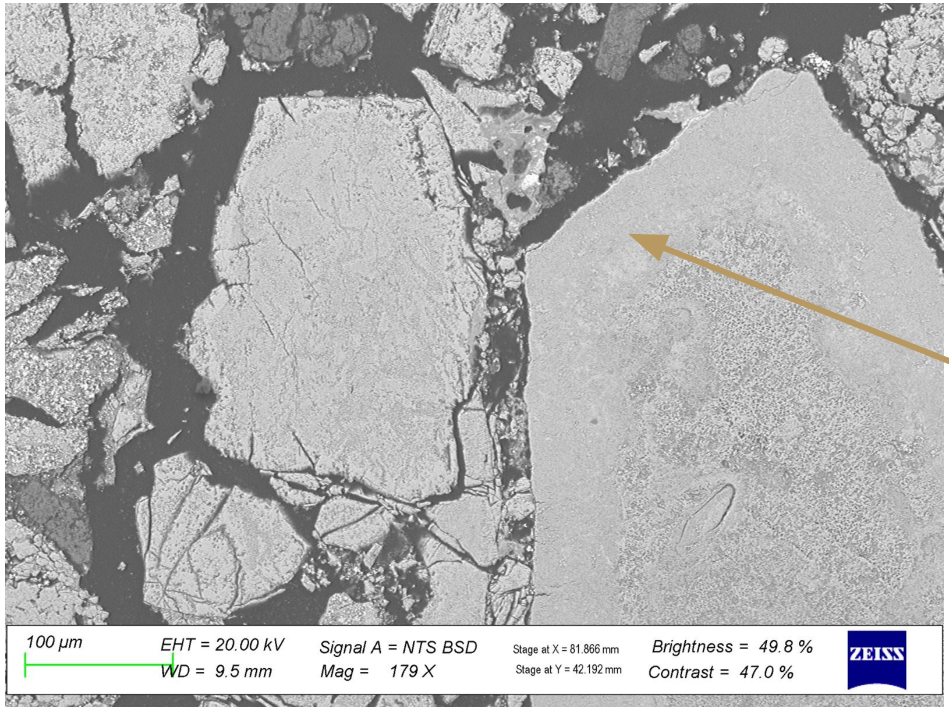
Runs 24 and 25(C): Full reduction (850 °C & 90% H_2 / 100% H_2)

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

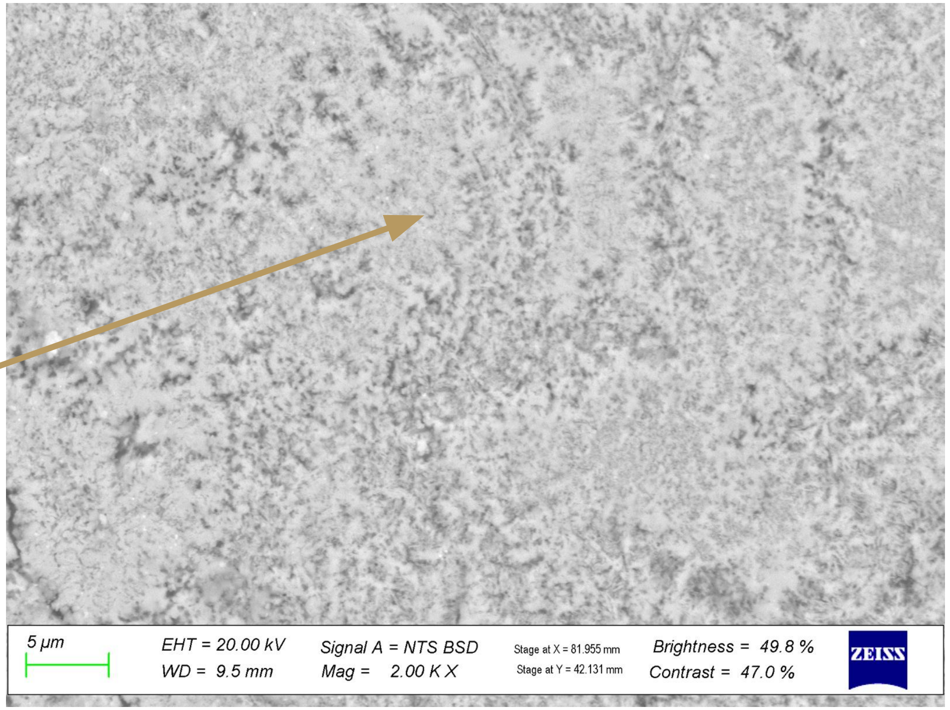
African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Highest Fe content with no flecks



Manganosite



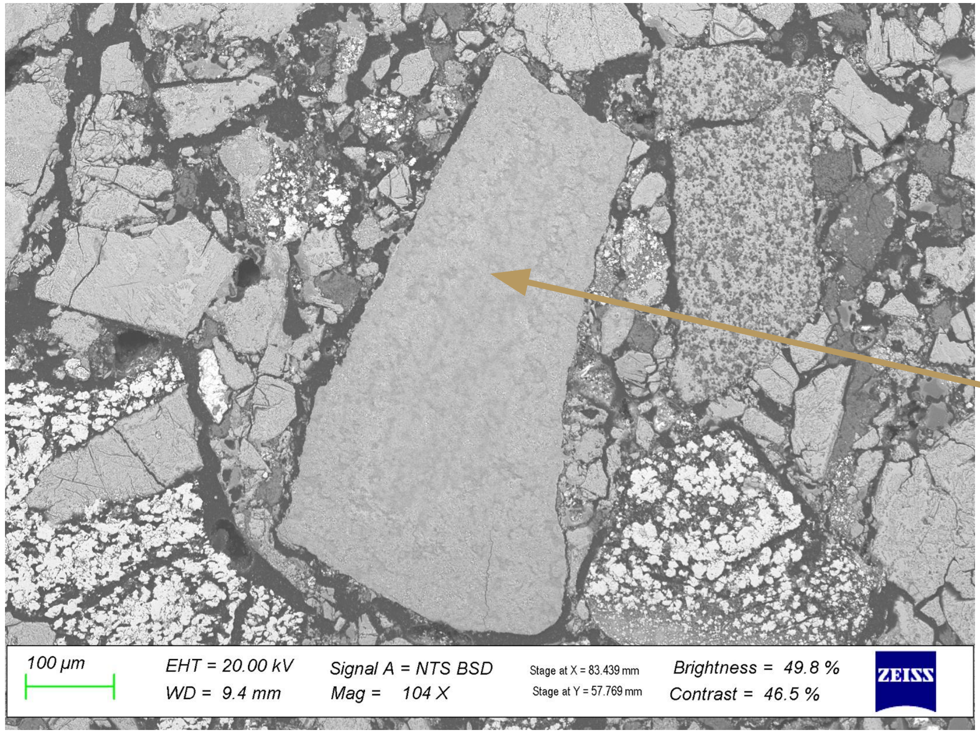
- Mn grain containing 13.1 mass % Fe
- Zoomed in

Stellenbosch University Iyunivesithi Universiteit

African Rainbow Minerals Chair in GeoMetallurgy

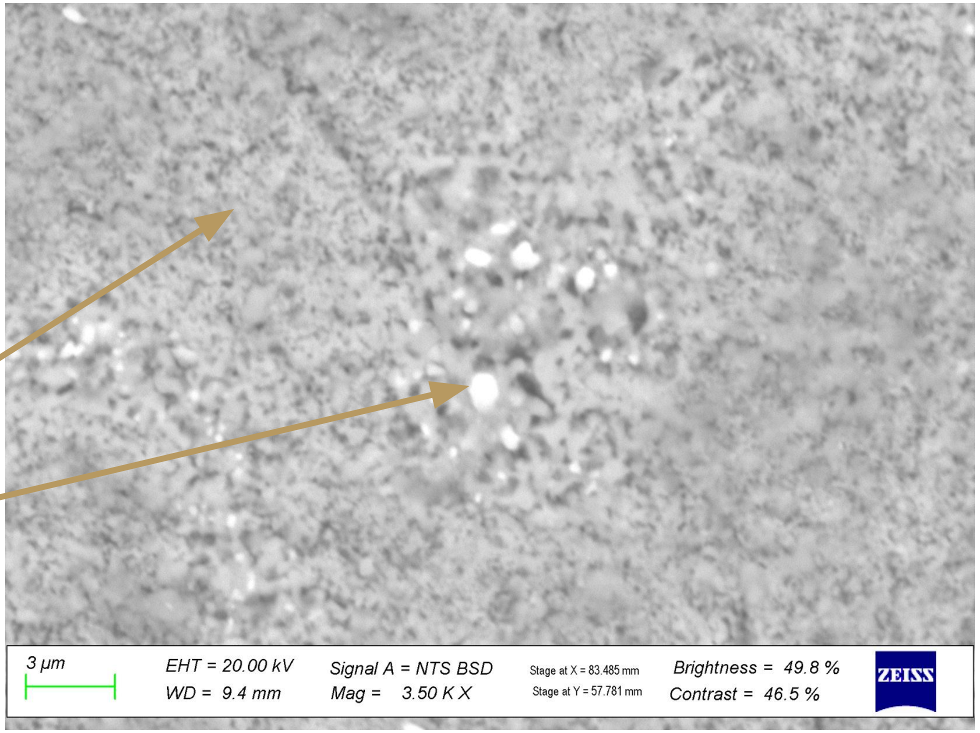
ARM African Rainbow Minerals

Initial flecks forming



Manganosite

Fe alloy



- Mn grain containing 13.6 mass % Fe
- Zoomed in

How Fe content & reduction conditions influence fleck formation

- Requires a higher Fe content to form flecks at milder reducing conditions

Run	Highest Fe bulk without fleck	Lowest Fe bulk with fleck
1	13.1%	13.6%
5	8.6%	16.8%
17	21.0%	62.2%
24	4.0%	7.4%
25(C)	5.4%	7.7%

Runs 1 and 5: Mildly reducing (750 °C & 85% H_2)

Run 17: Weakly reducing (650 °C & 90% H_2)

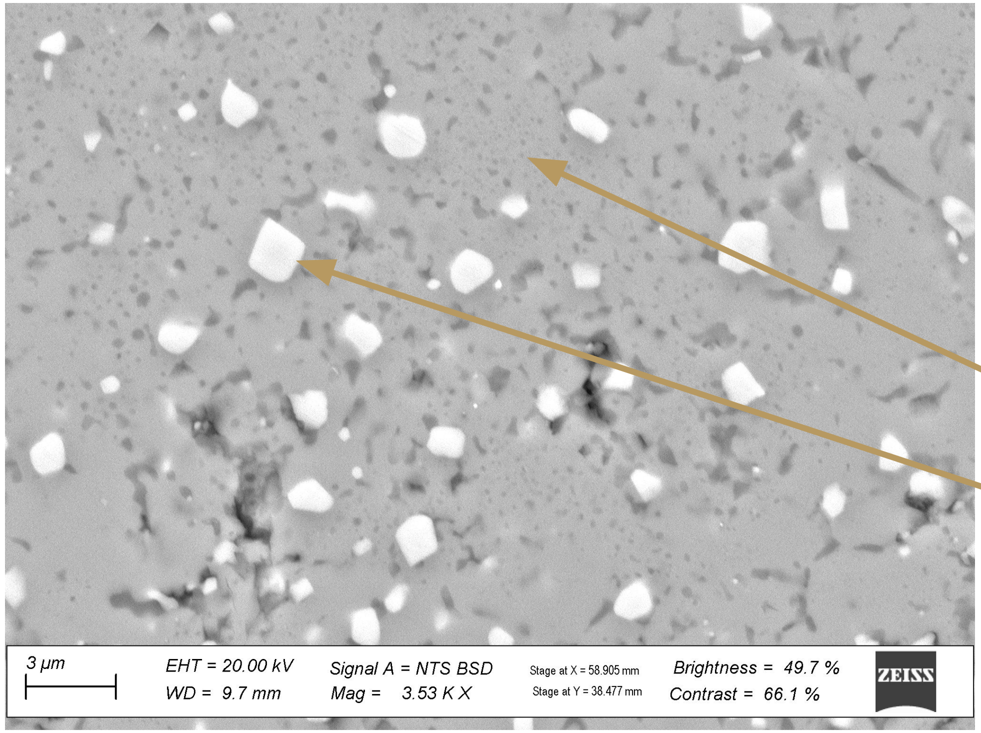
Runs 24 and 25(C): Full reduction (850 °C & 90% H_2 / 100% H_2)

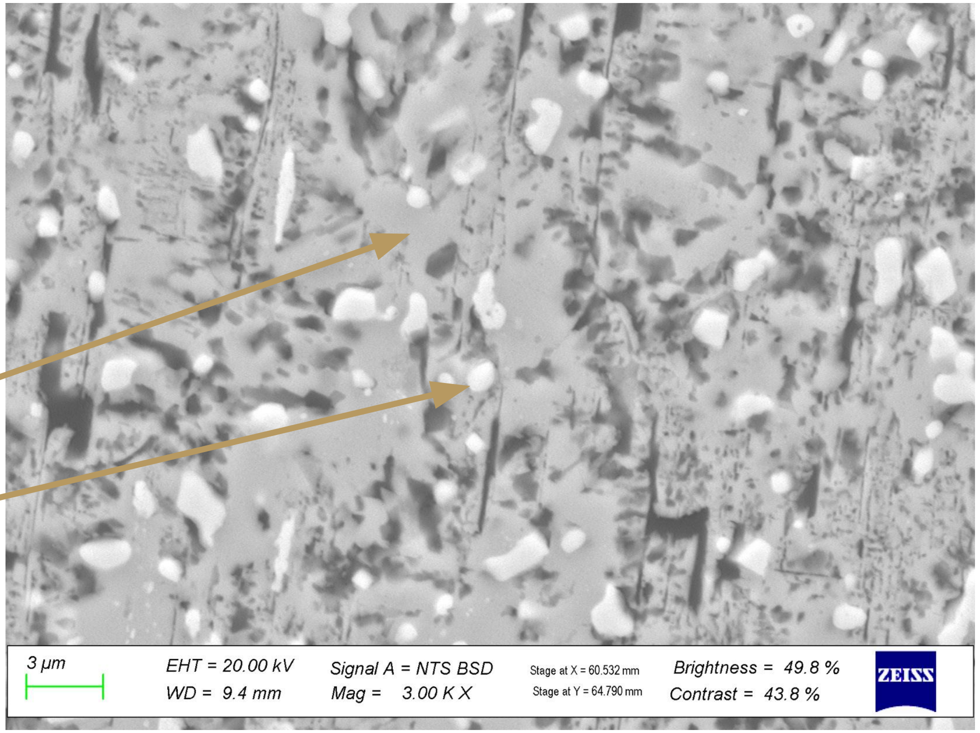
Stellenbosch University Iyunivesithi Universiteit

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Fe alloy flecks in treated bixbyite





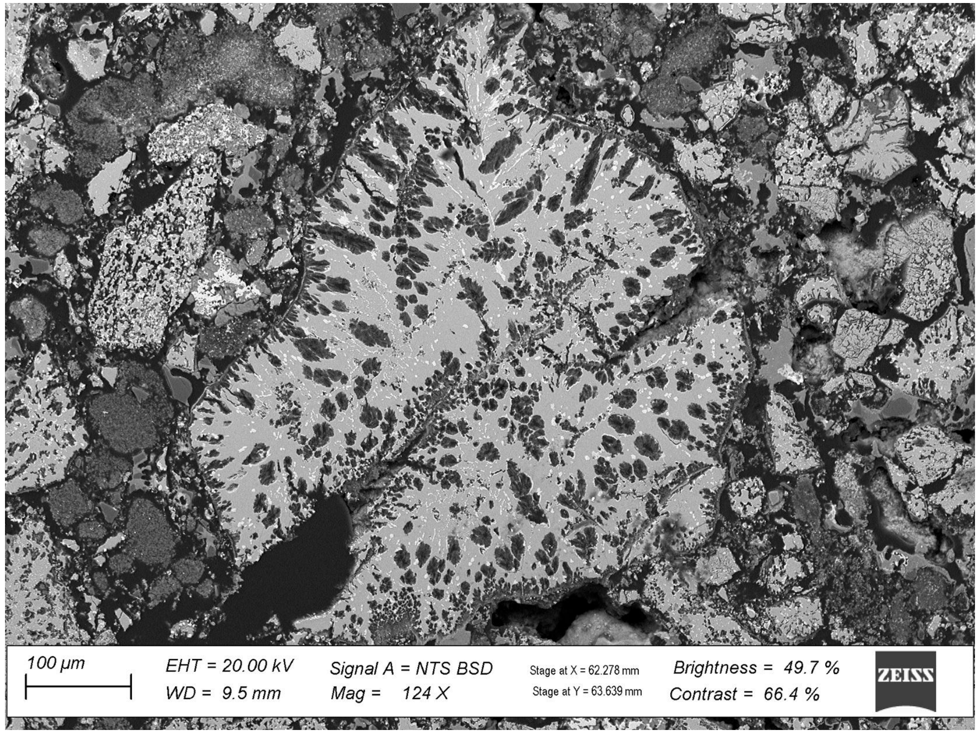
- Treated bixbyite reduced at 950 °C
- Treated bixbyite reduced at 850 °C

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

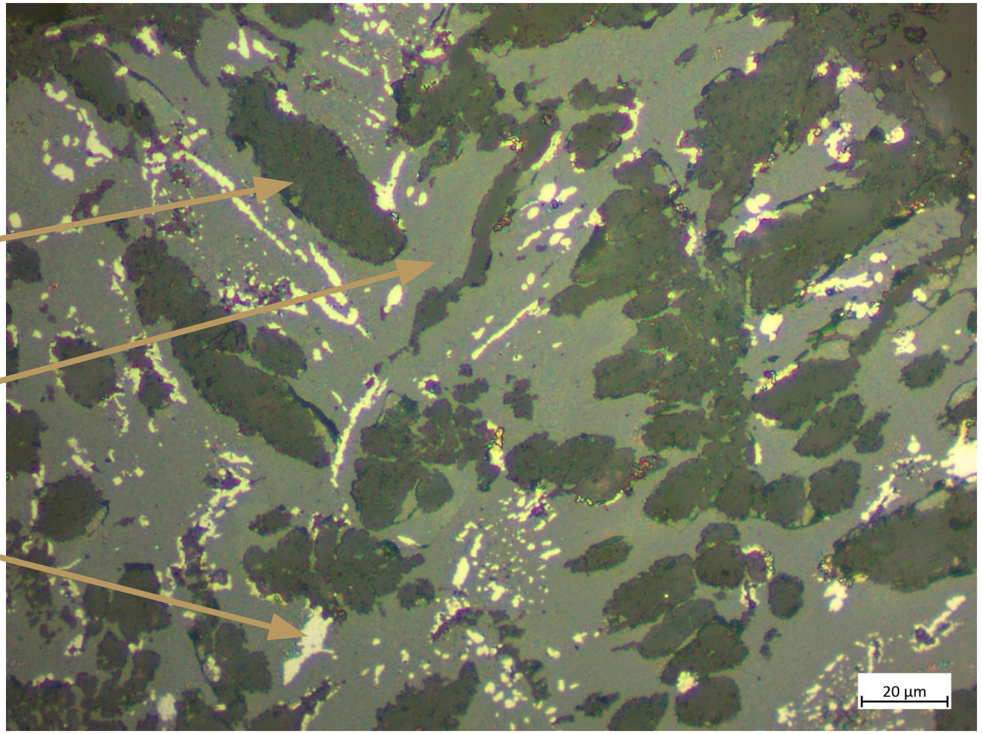
African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Braunite II new texture



- Reduced braunite II at 950 °C

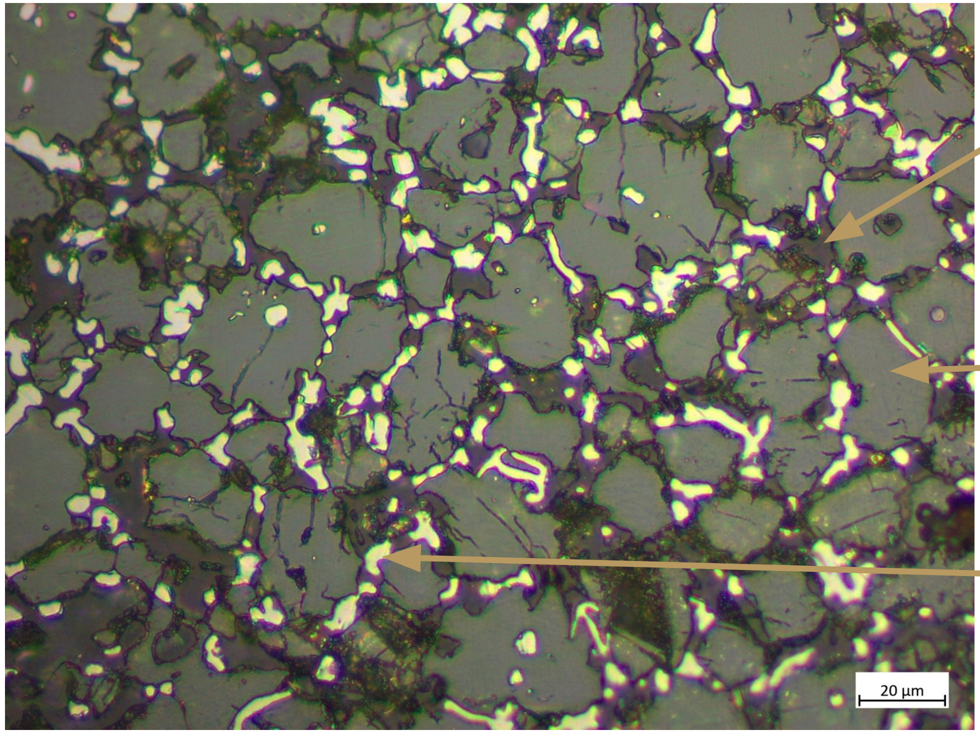


- Zoomed in using optical microscope

Stellenbosch University Iyunivesithi Universiteit
African Rainbow Minerals Chair in GeoMetallurgy
ARM African Rainbow Minerals

Same grain, increased reduction temperature

- Different texture
- Fe alloys well liberated from manganosite
- Possible to liberate Fe alloys through optimising crushing



Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Conclusions

- Hydrogen-rich reductive roasting → magnetic separation upgrades ferruginous Mn fines
  - Mn/Fe too low but can work with blending
  - Liberation and magnetic separation can be improved
- Milder reducing conditions resulted in better separability
- Minerals have unique reduction characteristics
  - Not able to take full advantage in current study

Thank you!

Questions?

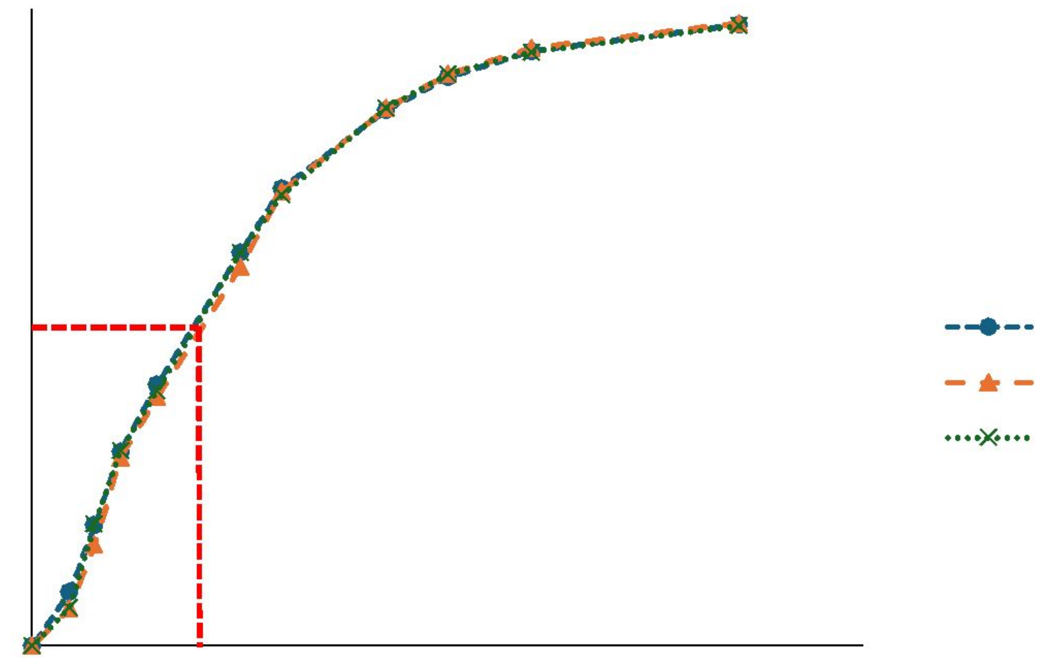
Photo by Stefan Els

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

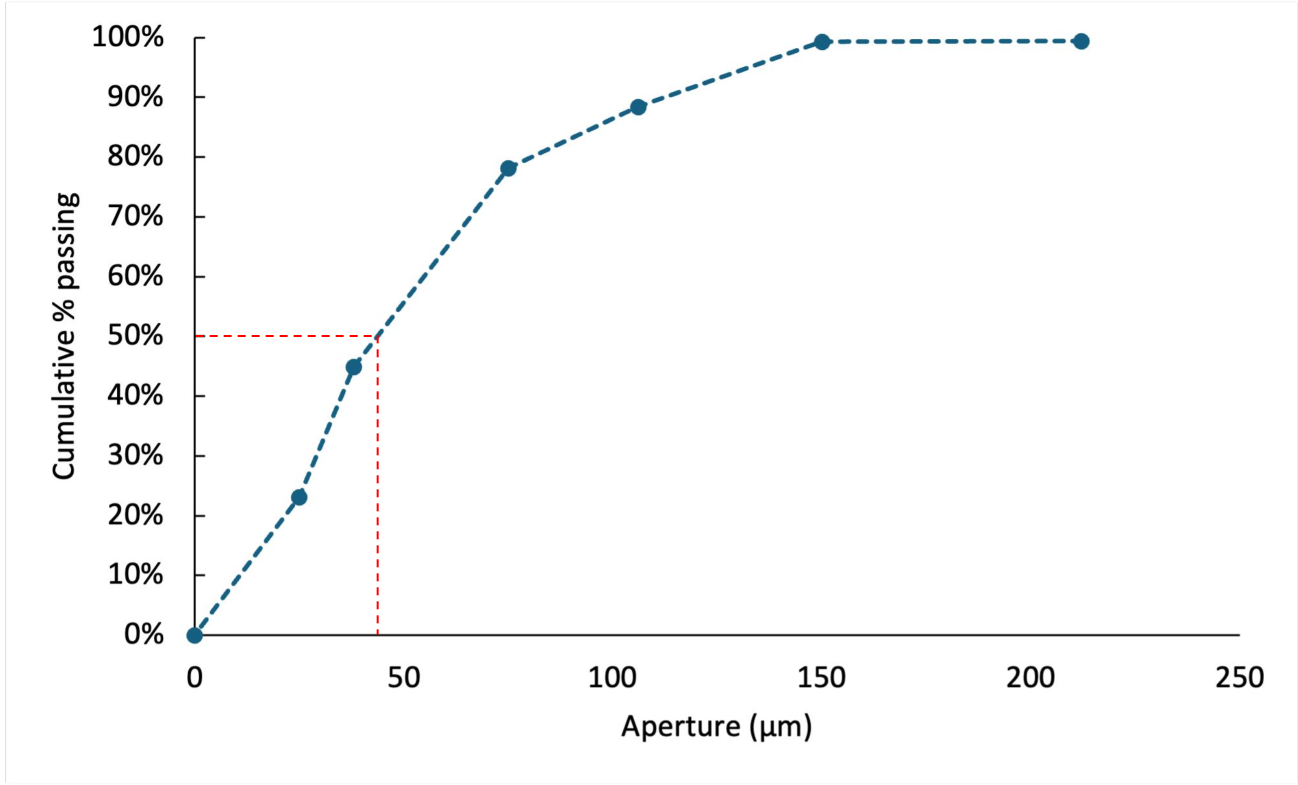
African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Particle size distribution - untreated



Particle size distribution - reduced and crushed

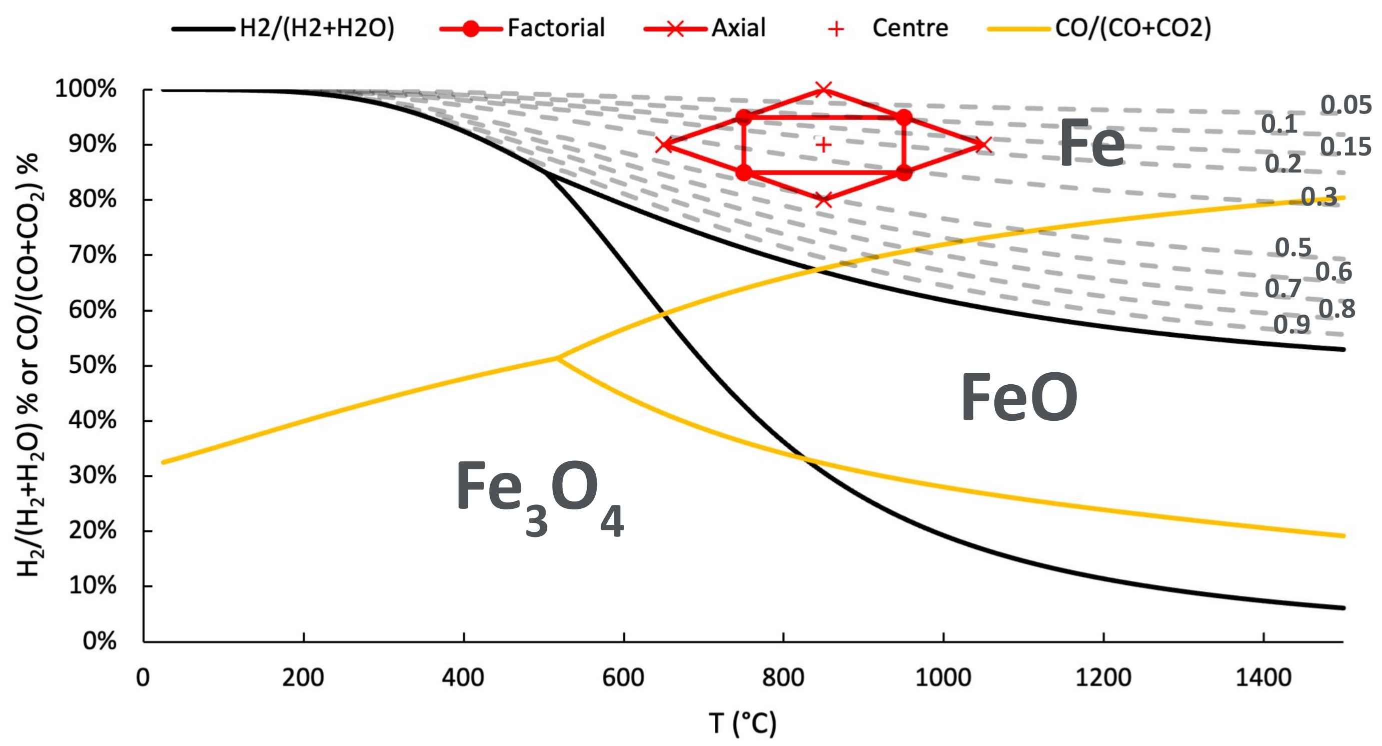


Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Iron oxides stability diagram



Stellenbosch University Iyunivesithi Universiteit

African Rainbow Minerals Chair in GeoMetallurgy

ARM African Rainbow Minerals

Back to mineralogy

- Significant differences in Mn/Fe possible for different minerals
  - Higher Mn/Fe for Braunite II at higher temps once new structure forms
- Not achieved in current study due to limits of liberation and magnetic separation
  - Improvement is possible

Mineral	Tailings Mn/Fe	Mn/Fe oxide
Bixbyite	7.88	9.02
Braunite	5.47	7.84
Braunite II	4.85	11.45