Hydrometallurgical upgrading of ferruginous manganese ore

By Mr E Olivier, Prof M Tadie, Prof B von der Heyden, Mr P van Wyk

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Recap: Manganese in SA

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Recognised as a "high-critical" mineral in SA, features in several critical mineral lists globally

KMD hosts nearly 80% of the global land-based Mn and has been used to produce FeMn since 1930's

Demand as battery-grade raw material is emerging but market share is small compared to FeMn

Recap: Ferruginous tailings

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- Hydrothermal alteration has enriched Mn but also Fe
- Ferruginous tailings have high Mn (>44%) but low Mn/Fe
- Magnetic separation is suboptimal due to mineralogy and texture

Combined Processing

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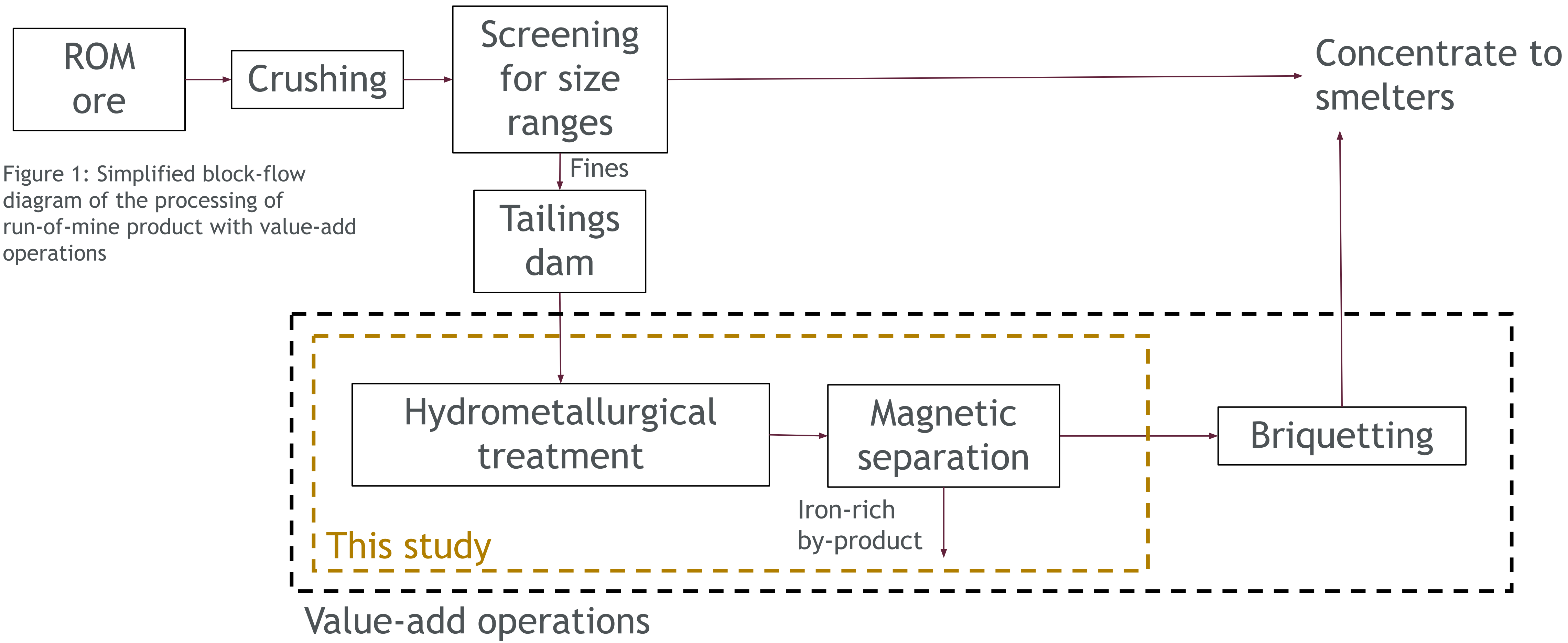

Figure 1: Simplified block-flow diagram of the processing of run-of-mine product with value-add operations

Dry magnetic separation of Fe & Mn minerals

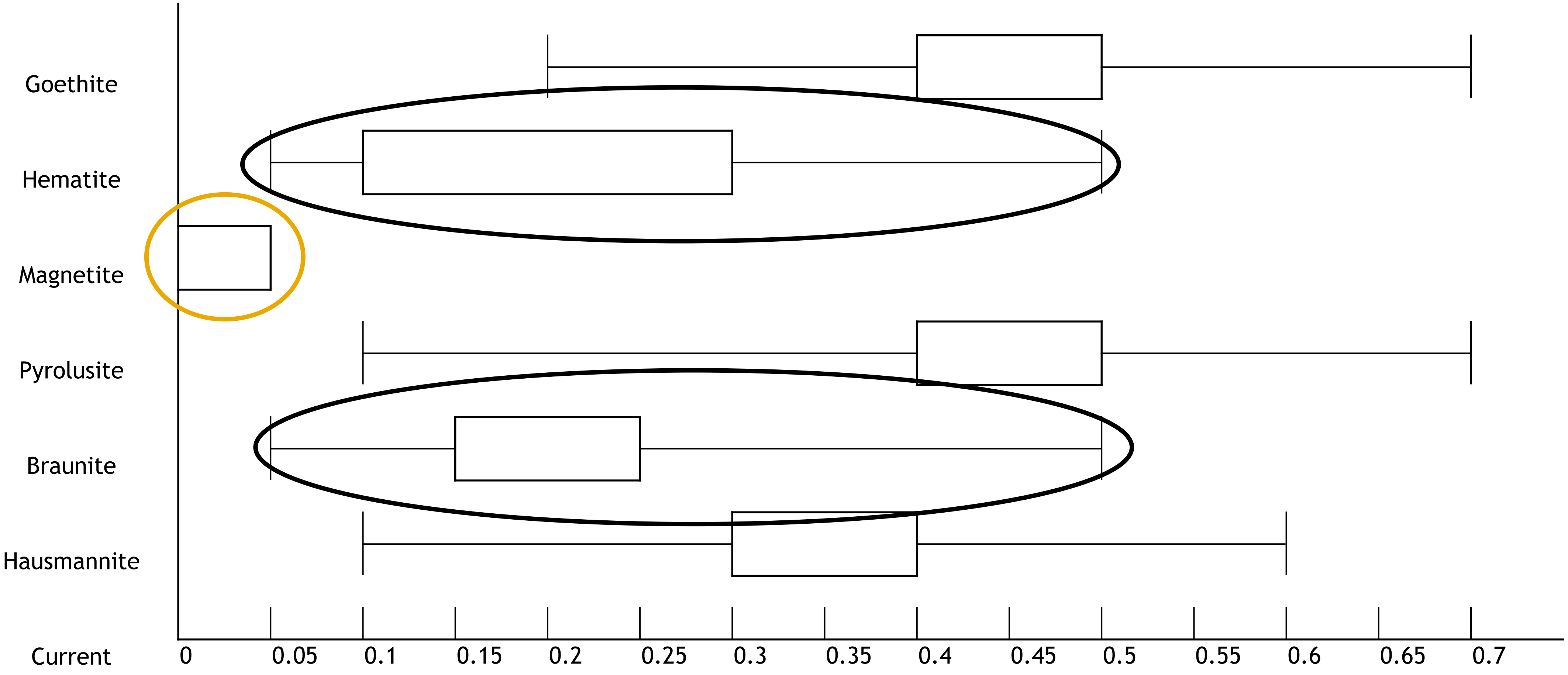

Figure 2: Total (lines) and optimal (boxes) current ranges for recovery of selected minerals (Rosenblum & Brownfield (2000))

Why is hematite not ferromagnetic?

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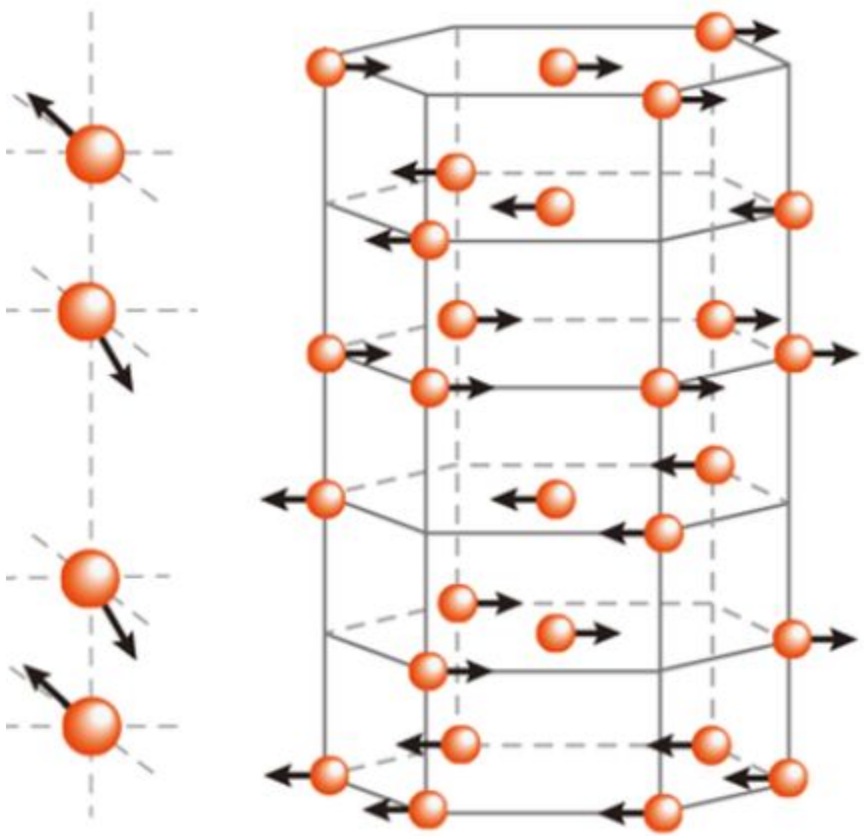

Figure 3: Magnetic structure of hematite (from Abrajevitch *et al* (2021))

Acid treatment

- Method proposed by Singh & Biswas (2017)
  - Tested on pyrolusite-based ore
  - Acidic leaching forms a fe-oxalate surface (Humboldtine)
  - Roasting converts the fe-oxalates to magnetic maghemite/magnetite

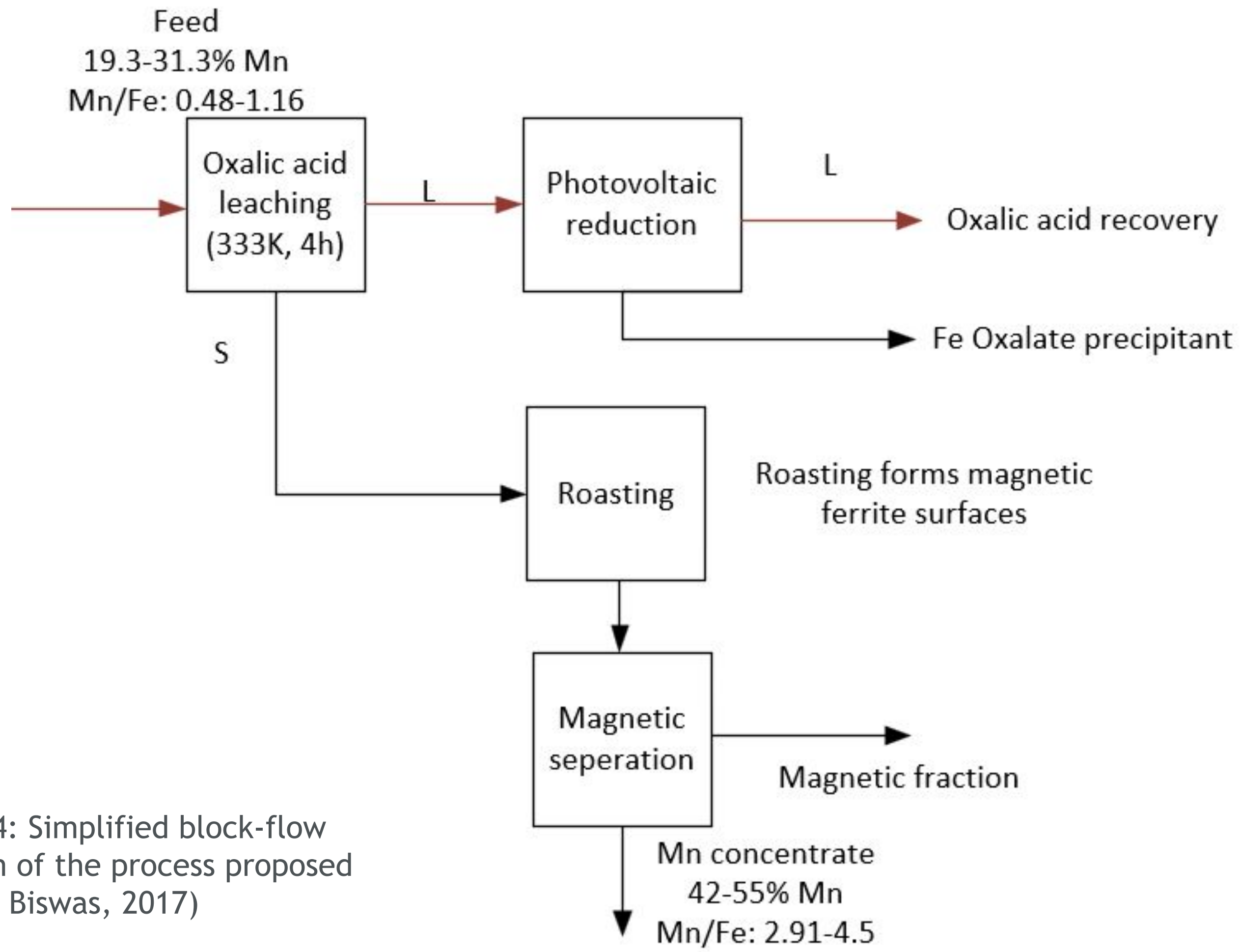

Figure 4: Simplified block-flow diagram of the process proposed Singh & Biswas, 2017)

Hematite - oxalic acid reaction

- $H_2C_2O_{4(aq)} \rightarrow 2H^+_{(aq)} + C_2O_{4(aq)}^{2-}$
- $Fe(III) - O_{(s)} + H^+ \rightarrow Fe(III) - OH^+{}_{(s)}$
- $Fe(III) - OH^+{}_{(s)} + C_2O_{4(aq)}^{2-} \rightarrow Fe(III)C_2O_{4(s)} + OH^-_{(aq)}$
- $Fe(III)C_2O_{4(s)} + Fe^{2+}_{(aq)} \rightarrow Fe(II)C_2O_{4(s)} + Fe^{3+}_{(aq)}$

- Acid dissociation
- Protonation
- Ligand substitution
- Autocatalysis
- Iron oxalate dissociation

(Source: Vehmaanperä et al., 2022)

Preliminary results: Acid treatment

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Manganese co-leaching was significant!

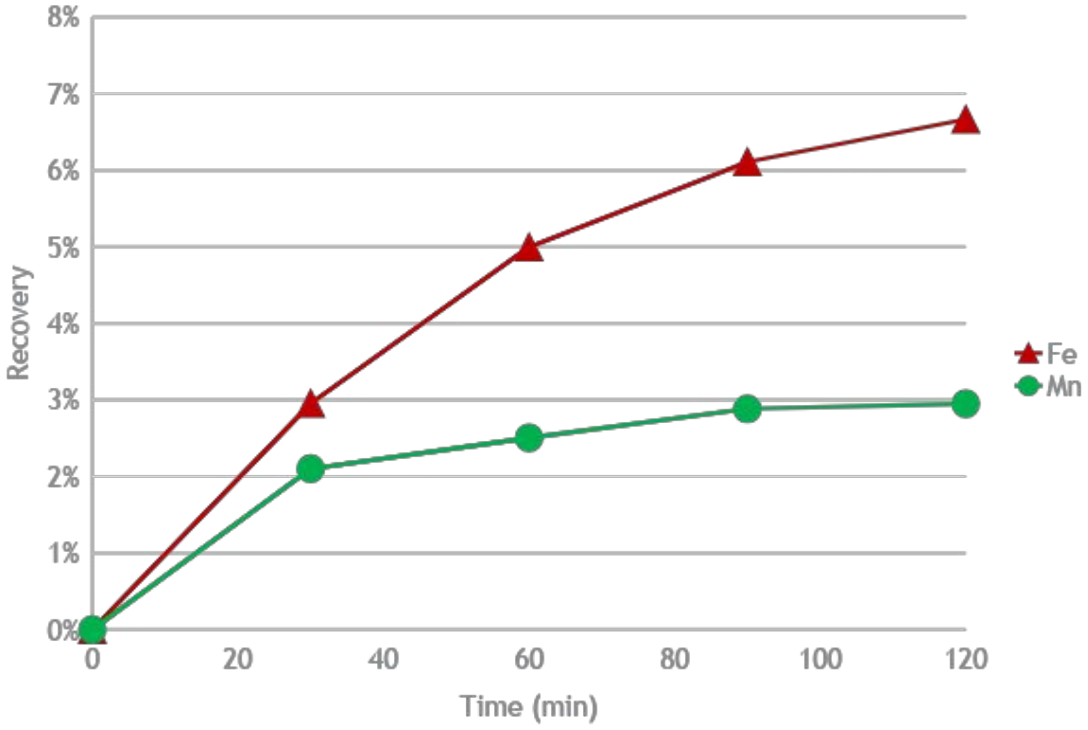

Figure 5: Percentage recovery of Fe & Mn to leach liquor

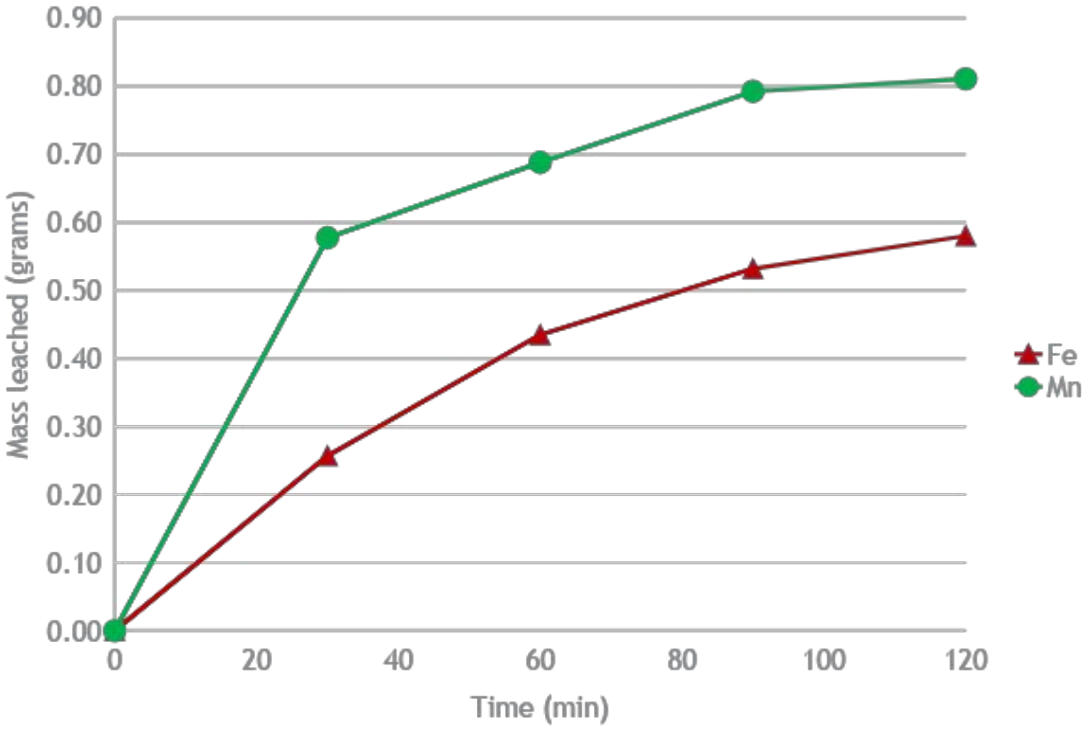

Figure 6: Amount of Fe & Mn recovered to leach liquor

Results: Why was Mn leaching significant?

- Process was identical to literature
- Mn grade was similar to literature
- Mn mineralogy was **NOT** similar to literature

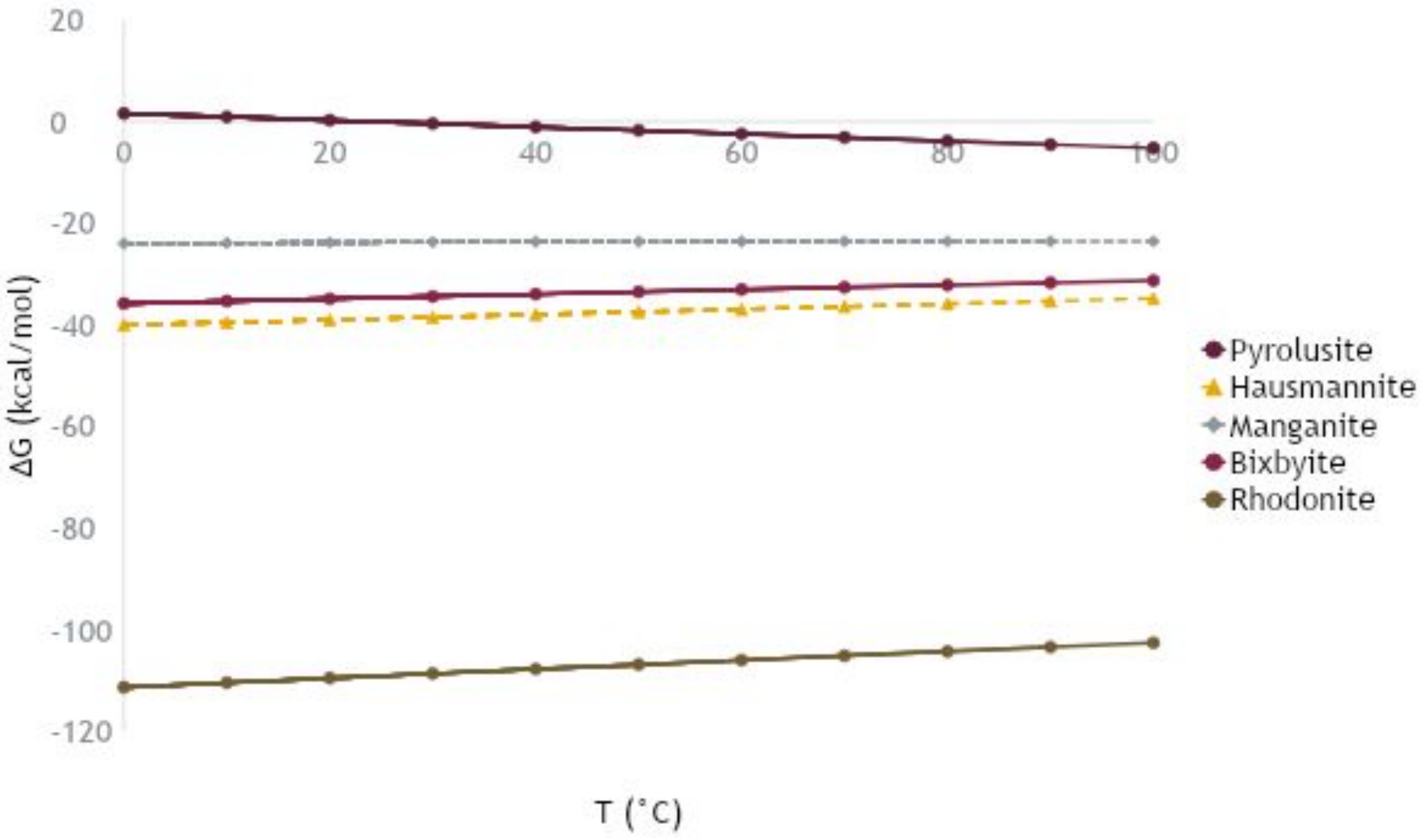

Figure 7: Gibbs Free Energy of Reaction plot for Fe and Mn mineral dissolution reactions in acidic media

Preliminary results: Acid treatment

- Roasted residue showed higher magnetism
- Achieved Mn/Fe = 2.98

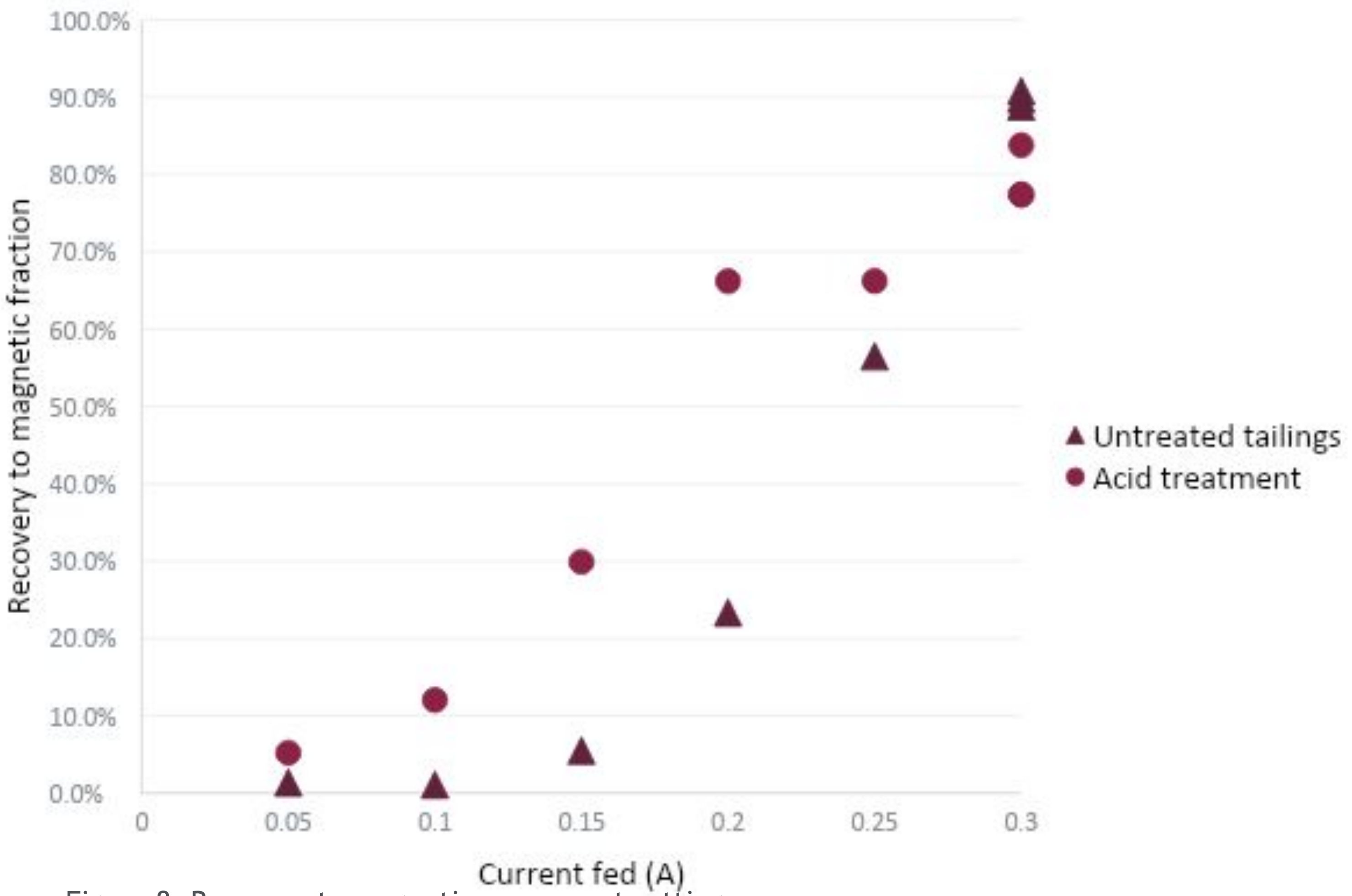

Figure 8: Recovery to magnetics vs current setting

Oxalic acid treatment: CCD experimental design

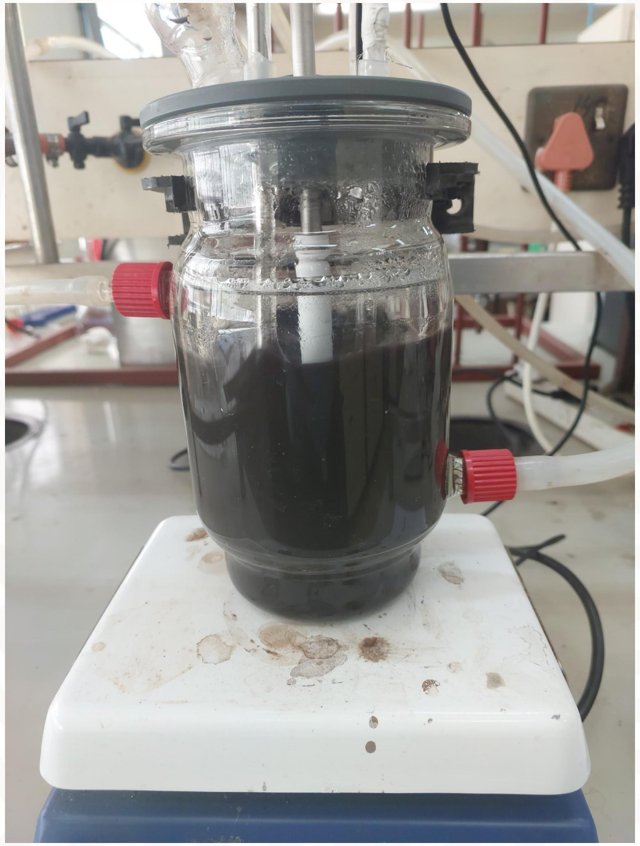

Figure 9: Leaching of tailings in oxalic acid

- Design based on Temperature, Duration, and Concentration
- 3-factor, 2-level central composite design (CCD)

Table 4: Parameters for Acid Treatment CCD

Variable	-α	-1	Centre point	+1	+α
Temperature (°C)	70	75	82.5	90	95
Acid concetration (M)	0.08	0.25	0.5	0.75	0.92
Duration (minutes)	70	90	120	150	170

Acid CCD: Statistical analysis

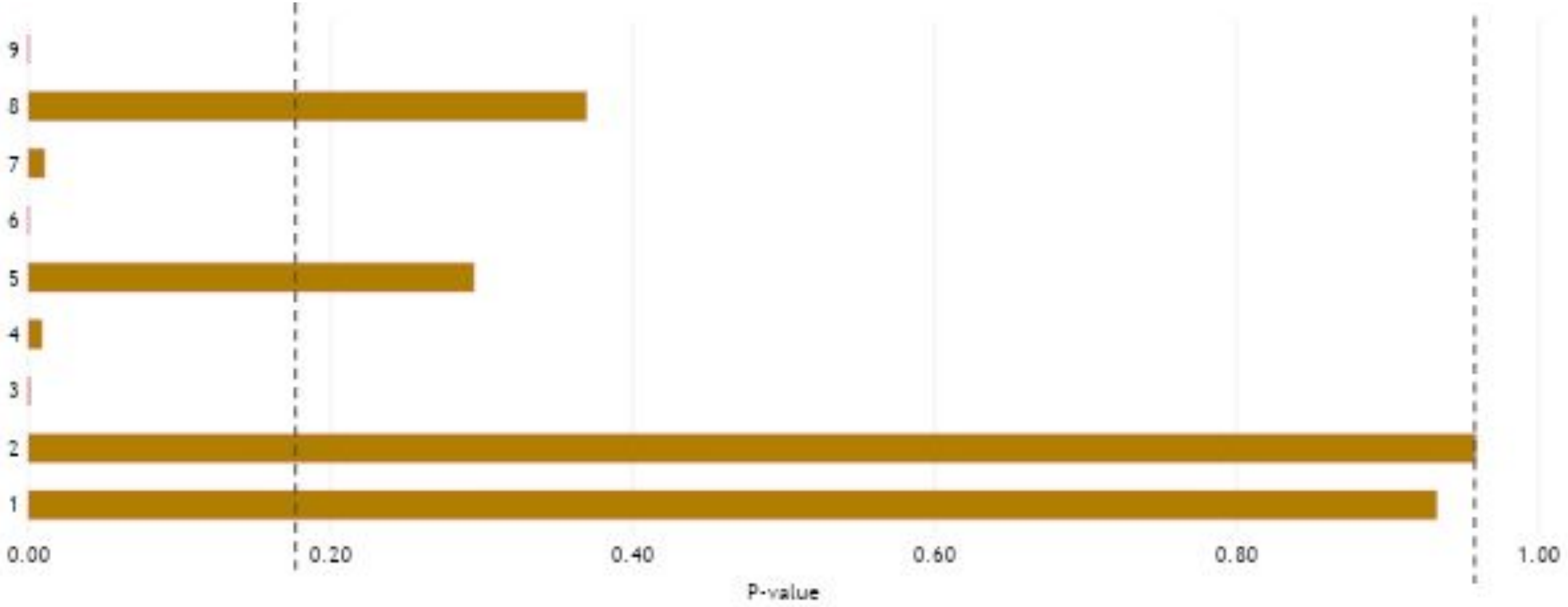

Figure 10: Pareto diagram from statistical analysis of leaching experiments

Acid CCD: Leaching models

	R^2 = 0.94
	R^2 = 0.91
	R^2 = 0.68

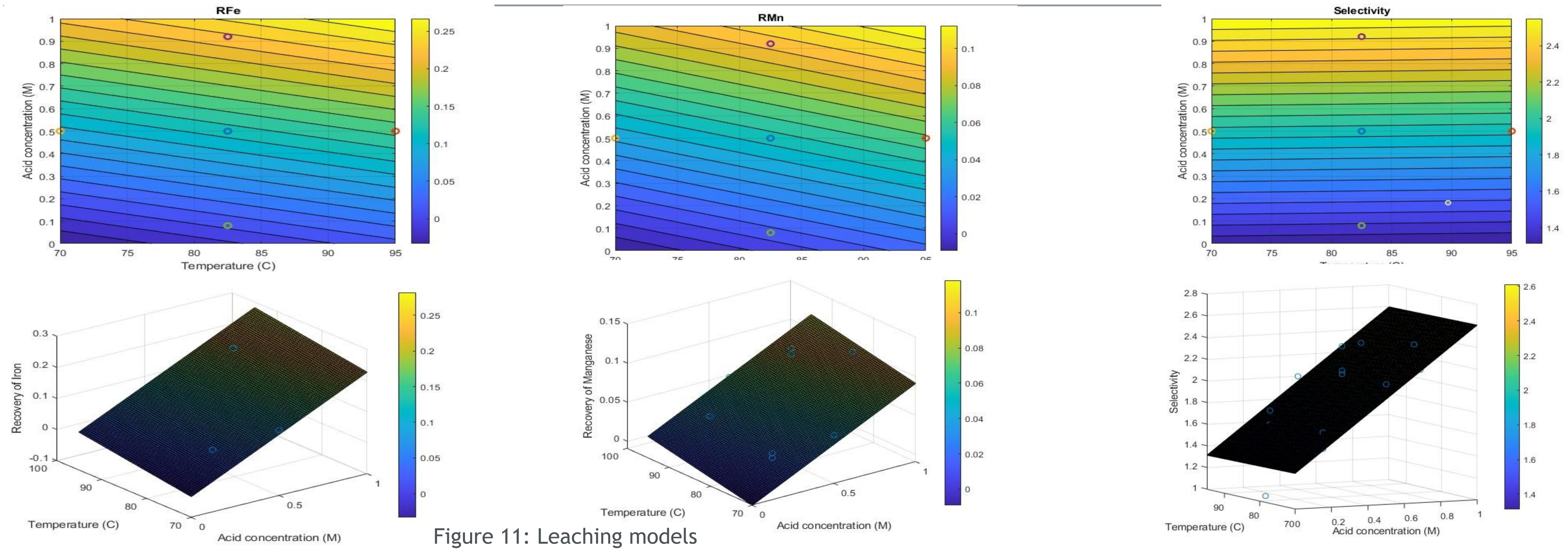

Figure 11: Leaching models

Acid CCD: Magnetic separation

- Acid concentration showed significant positive correlation with recovery and Mn/Fe
- Reaction time did not influence recovery or Mn/Fe significantly
- Recovery could be modelled well by predictors (R^2 = 0.60), but Mn/Fe showed considerably worse fit (R^2 = 0.36)
- Maximum Mn/Fe of 3.65

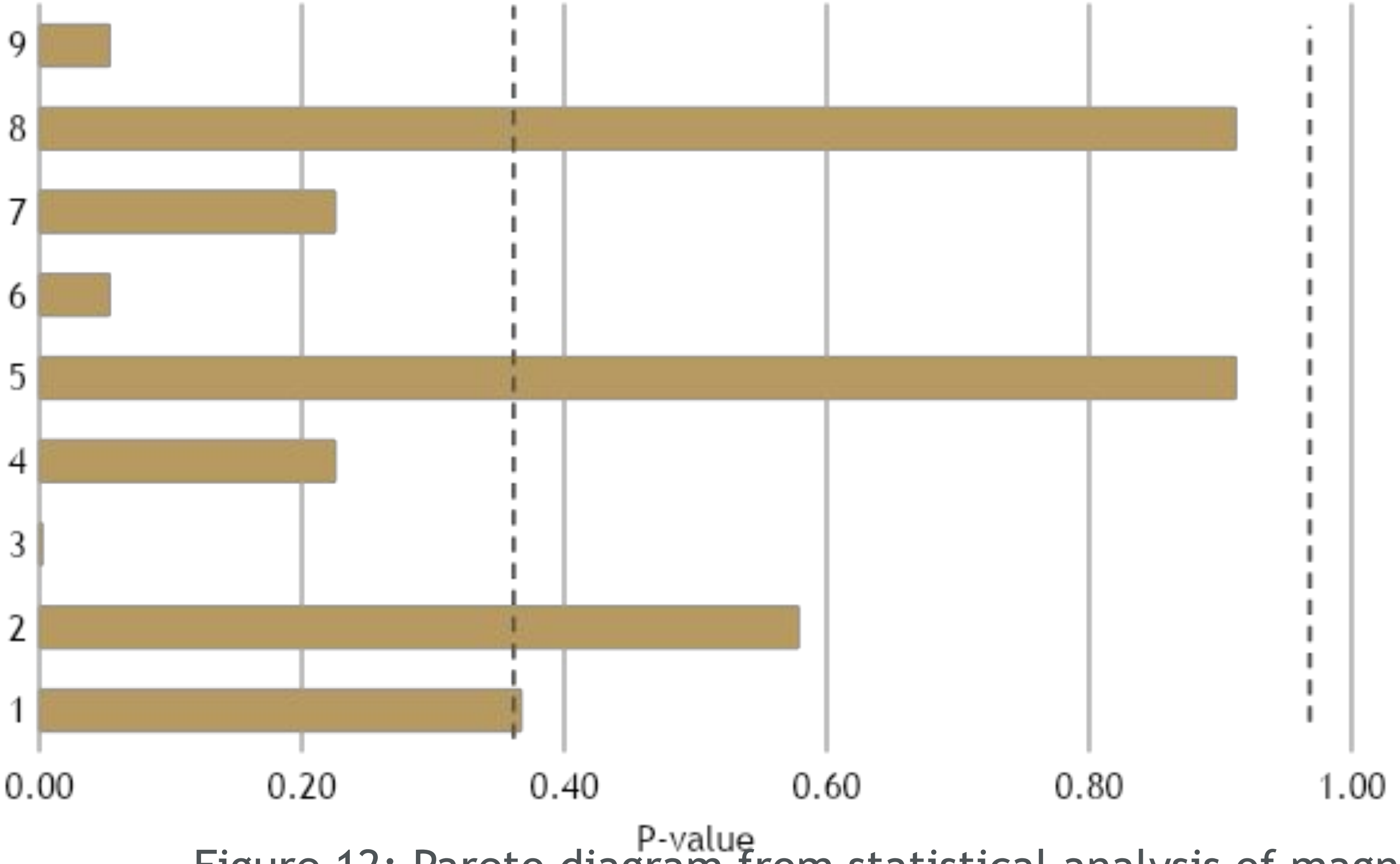

Figure 12: Pareto diagram from statistical analysis of magnetic separation experiments

Base treatment

- Originally autoclave process (Pasechnik *et al*, 2020)
- Proven to work at ambient pressure (Zhou *et al*, 2023)
- Originally proposed for treatment of alumina production residues

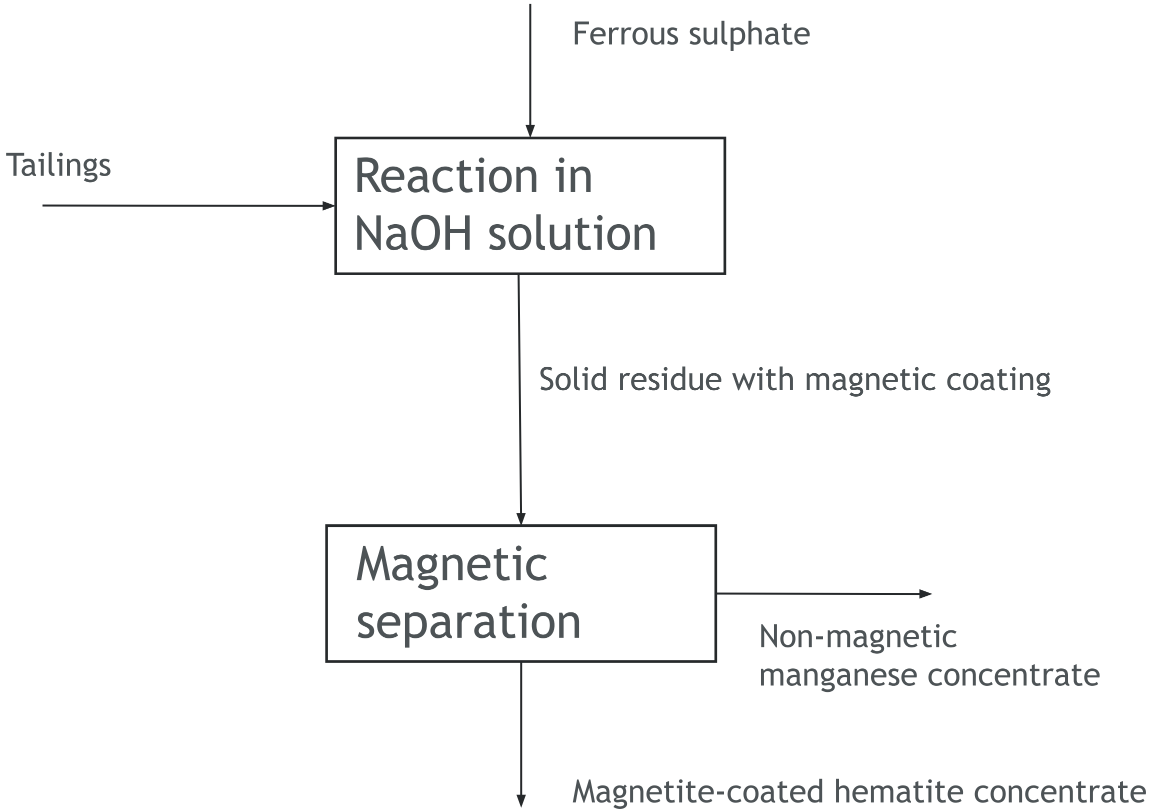

Figure 13: Simplified block-flow diagram of the process proposed Zhou *et al*, 2023)

Base treatment

- Presence of magnetite was confirmed via XRD
- Method did not increase selectivity

Table 1: Results of magnetic separation of base treated tailings vs untreated tailings

Sample	Untreated tailings			Base treatment		
Field setting	Recovery	Mn/Fe		Recovery	Mn/Fe	
		Mags	Non-mags		Mags	Non-mags
0.1	1.1%	2.62	2.62	1.0%	1.86	2.66
0.15	5.5%	2.97	2.62	18.8%	2.71	2.29
0.2	23.3%	2.72	1.81	28.8%	2.87	2.41
0.25	56.5%	2.01	3.03	47.7%	2.81	2.61

Base treatment: Why didn't it work?

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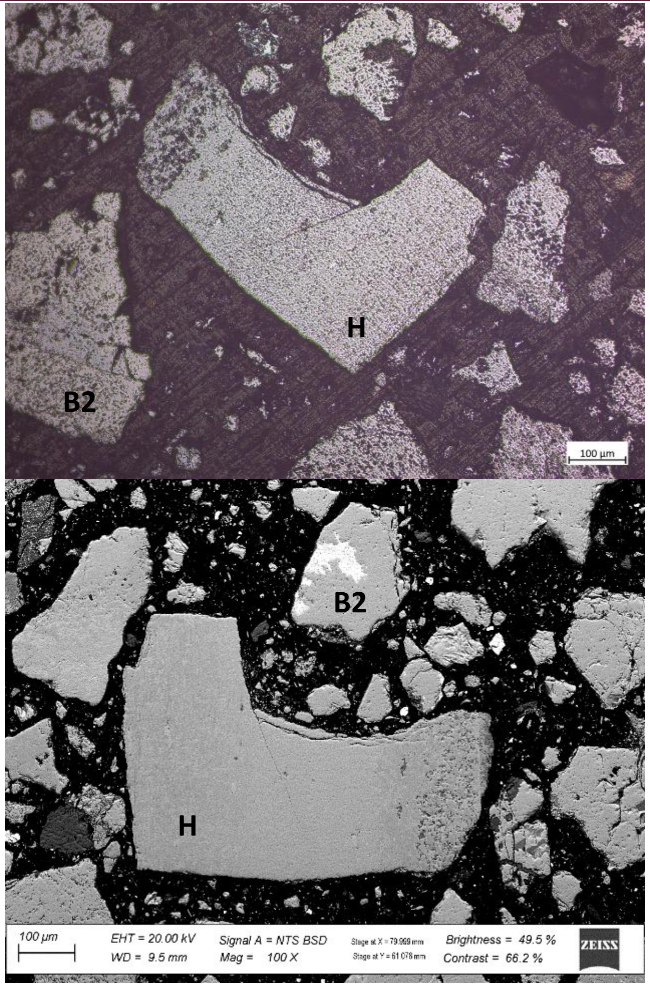

Figure 14: Optical and SEM Images of oxide particles (H- hematite, B2 – Braunite II)

Table 2: Chemical analysis via SEM-EDS of mineral grains

Spectrum Label	H - hematite	B2 - Braunite II
O	25.68	25.48
Mg		0.41
Si	0.91	1.63
Ca	0.65	2.10
Mn	14.12	60.09
Fe	58.64	10.29
Total	100.00	100.00

- Iron is too finely associated with Mn in mixed oxide grains
- Liberation is required

Conclusions

More value can be unlocked from deposits with integrated beneficiation

- Can create multiple value fractions from one waste

Can't rely on just geochemistry in hydrometallurgy

- Mineralogy dictates dissolution reactions
- Texture can make-or-break physical beneficiation

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Thank you
Enkosi
Dankie

Photo by Stefan Els

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Acid scoping Mn/Fe

	Untreated tailings			Acid treatment		
		Mn/Fe			Mn/Fe	
Field setting	Recovery	Magnetic	Non-magnetic	Recovery	Magnetic	Non-magnetic
0.1	1.1%	2.62	2.62	12.0%	1.66	2.85
0.15	5.5%	2.97	2.62	29.9%	1.97	3.32
0.2	23.3%	2.72	1.81	66.2%	2.51	2.80
0.25	56.5%	2.01	3.03	66.2%	2.48	2.60
0.3	88.8%	2.83	2.40	83.8%	1.50	2.77

Reactions - full