Hydrometallurgical Recycling: Black Mass leaching performance – a combined experimental and regression modelling approach

Cluster Hub Annual Meeting

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RESPECT NUMBERS AND FIGURES

European Climate, Infrastructure and Environment Executive Agency
Project number: 101069865

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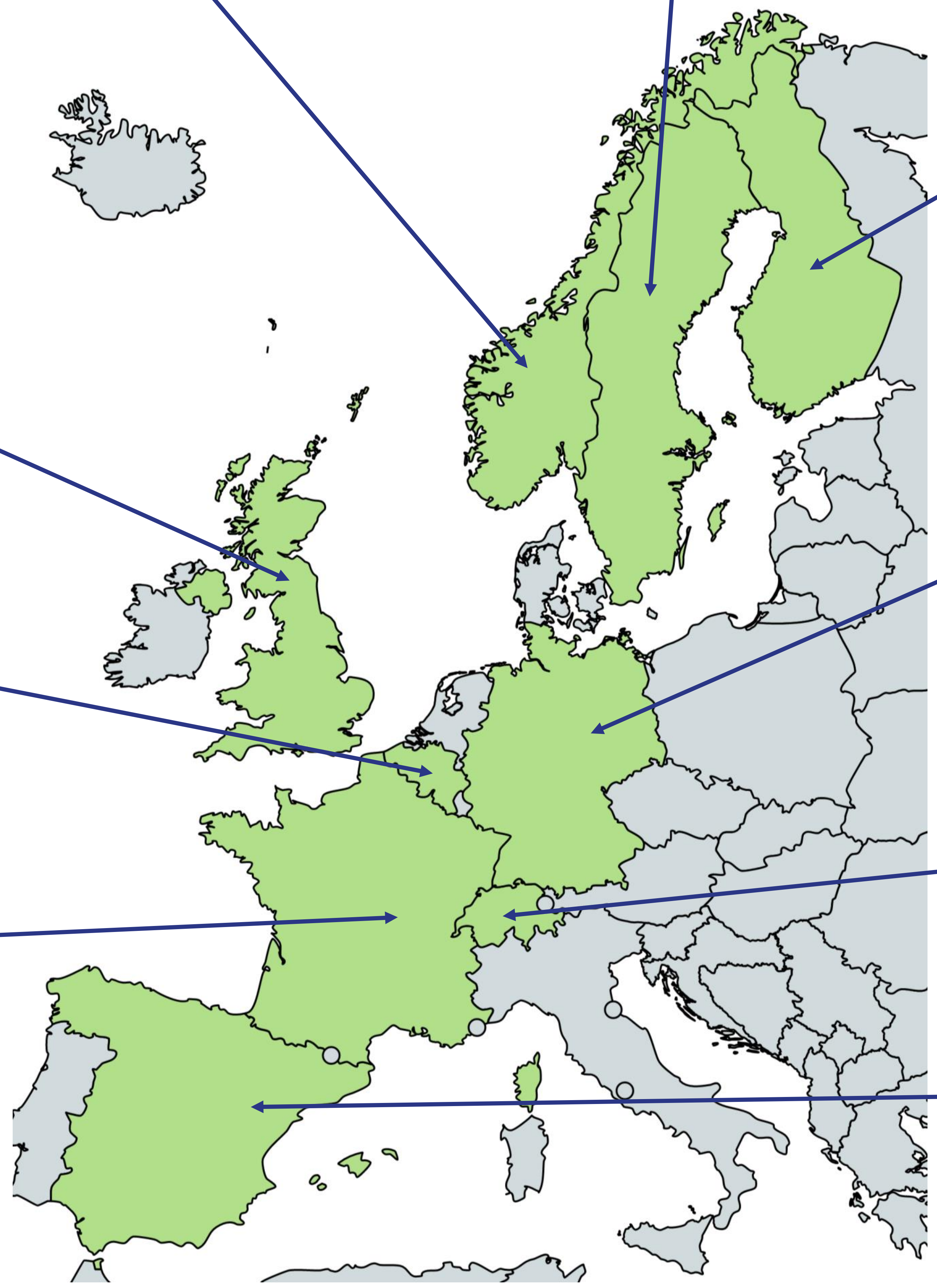

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RESPECT OVERVIEW

RESPECT's aim is to achieve efficient, sustainable, innovative and safe battery recycling processes in the EU encompassing new processes capable of achieving > 90% wt recovery rate/efficiency and supporting Li-ion battery manufacturing in Europe.

OUR OBJECTIVES

- Implementing efficient logistic solution for Li-ion batteries management and sorting
- Full recovery and high valorisation of resources within batteries
- Enabling LiBs safe deactivation at the industrial scale while limiting environmental impact, raw material resources and cost
- Low CO_2 hydrometallurgy
- Using innovative separation technologies for improving active materials access
- Improved life Cycle Assessment of each segment of the battery value chain
- Innovative and low-carbon direct recycling

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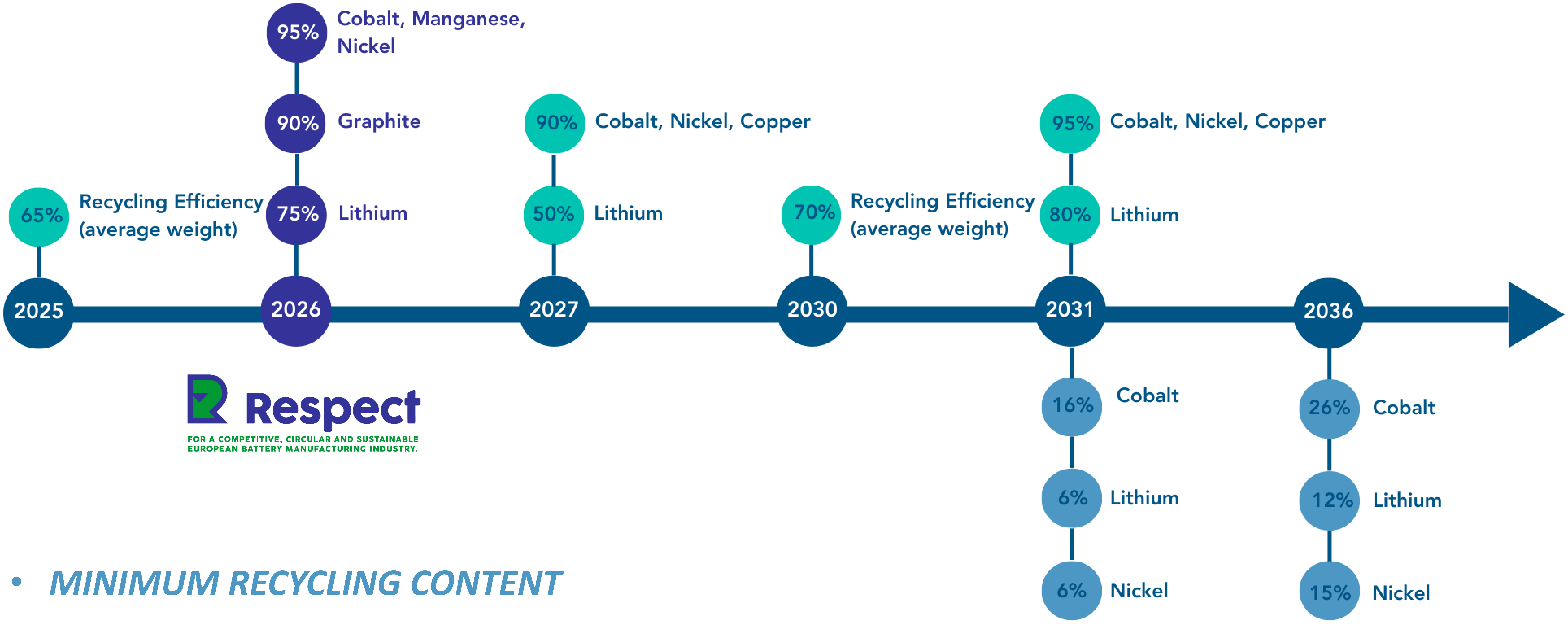
BATTERY REGULATION TARGETS AND RESPECT RECOVERY TARGET



- *MINIMUM RECYCLING CONTENT*

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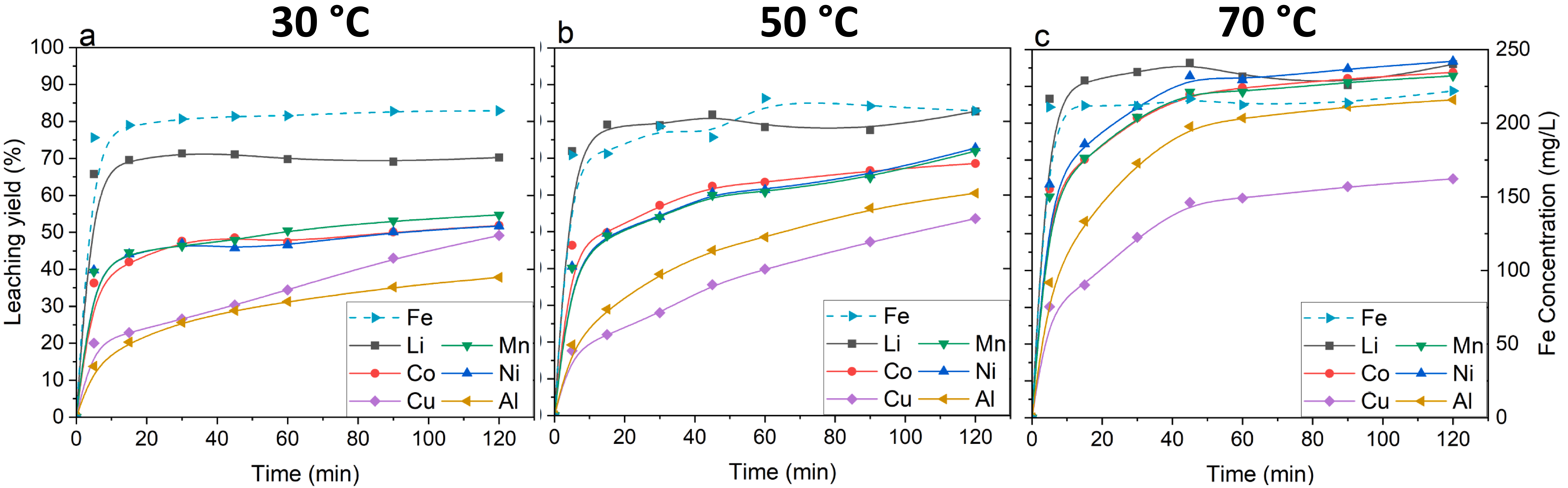
Methodology

- Parameters
  - 2M H_2SO_4 (Lixiviant)
  - Industrial Black Mass (NMC111)

Element	Li	Co	Ni	Mn	Cu	Al	Fe
Average	3.3	10	8.8	7.9	7.5	3.5	0.1
Standard deviation	0.08	0.55	0.36	0.21	1.35	0.18	0.02

- Investigated Reductants
  - $FeSO_4 \cdot 7H_2O$ (Fe^{2+})
  - Ground metallic copper recovered from spent battery electrodes
  - 50% H_2O_2

Effect of Temperature on Black Mass Leaching



- **Increasing temperature results in higher leaching yields for all metals**
- **Yields > 90% achieved for target elements (Li, Mn, Co, Ni) at 70 °C**
- **However, relatively high temperature for industrial operation Can temperature be reduced, whilst maintaining leaching yields?**
- **→ Use of reductants: Hydrogen peroxide (H_2O_2), Cu, Fe, Al**

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Use of Alternative Reductants

- $4LiCoO_{2(s)} + 6H_2SO_{4(aq)} \rightarrow 2Li_2SO_{4(aq)} + 4CoSO_{4(aq)} + 6H_2O_{(l)} + O_{2(g)}$

- $6LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2(s)} + 18H^+_{(aq)} + 3H_2O_{2(aq)} \rightarrow 6Li^+_{(aq)} + 2Ni^{2+}_{(aq)} + 2Mn^{2+}_{(aq)} + 2Co^{2+}_{(aq)} + 12H_2O_{(l)} + 3O_{2(g)}$

- $2LiCoO_{2(s)} + Cu_{(s)} + 8H^+_{(aq)} \xrightarrow{Fe(II)/Fe(III)} 2Li^+_{(aq)} + 2Co^{2+}_{(aq)} + 4H_2O_{(l)} + Cu^{2+}_{(aq)}$

- $3LiCoO_{2(s)} + Al_{(s)} + 12H^+_{(aq)} \xrightarrow{Fe(II)/Fe(III)} {}_{Fe(II)/Fe(III)}\, 3Li^+_{(aq)} + 3Co2^+_{(aq)} + 6H_2O_{(l)} + Al^{3+}_{(aq)}$

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Design of Experiments (DoE)

DOE series							
Exp. Number	Fe level	Cu level	H2O2 level	FeSO4·7H2O (g)	Cu (g)	H2O2 (ml)	T (°C)
A5	0	0	0	0,0	0,00	0	30
A21	1	0	0	0,5	0,00	0	30
A23	2	0	0	1,0	0,00	0	30
A24	0	1	0	0,0	7,48	0	30
A25	1	1	0	0,5	7,48	0	30
A26	2	1	0	1,0	7,48	0	30
A27	0	0	1	0,0	0,00	6,7	30
A28	1	0	1	0,5	0,00	6,7	30
A29	2	0	1	1,0	0,00	6,7	30
A30	0	1	1	0,0	7,48	6,7	30
A31	1	1	1	0,5	7,48	6,7	30
A32	2	1	1	1,0	7,48	6,7	30
A33	0	0	0	0	0	0	50
A34	1	0	0	0,5	0	0	50
A35	2	0	0	1,0	0	0	50
A36	0	1	0	0	7,48	0	50
A37	1	1	0	0,5	7,48	0	50
A38	2	1	0	1,0	7,48	0	50
A39	0	0	1	0	0	6,7	50
A40	1	0	1	0,5	0	6,7	50
A41	2	0	1	1,0	0	6,7	50
A42	0	1	1	0	7,48	6,7	50
A43	1	1	1	0,5	7,48	6,7	50
A44	2	1	1	1,0	7,48	6,7	50

- Design of experiments (DoE) is a statistical tool designed to allow for the assessment of interaction effects between multiple studied variables
- DoE methodology and regression modeling were used to construct models able to predict leaching yields from industrial black mass
- Parameters selected for investigation included:
  - Temperature,
  - Fe concentration
  - Additions of Cu, Al, and H_2O_2
- Models fitted using the partial least squares method

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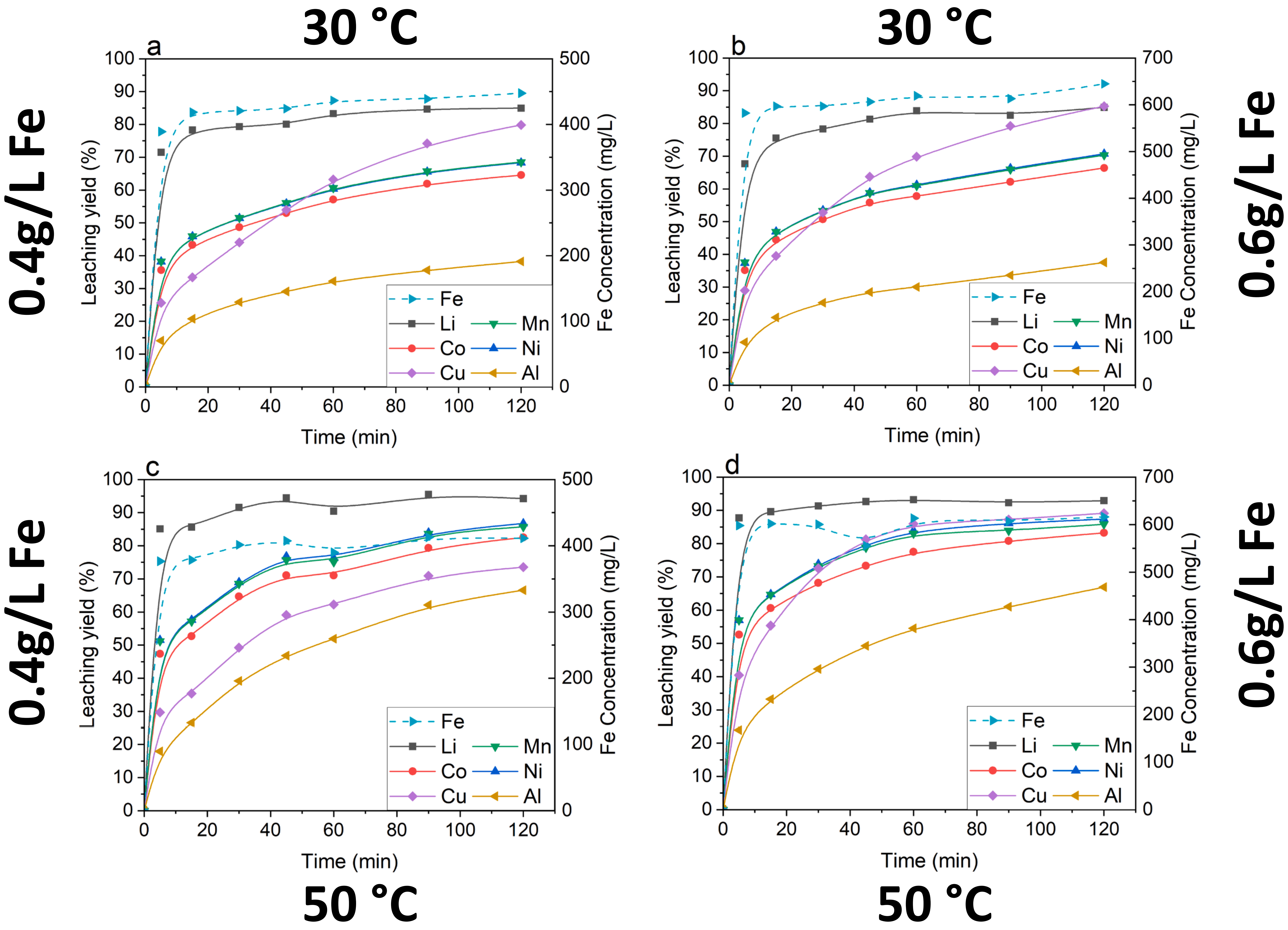
Example: Effect of Added Iron Reductant on Leaching



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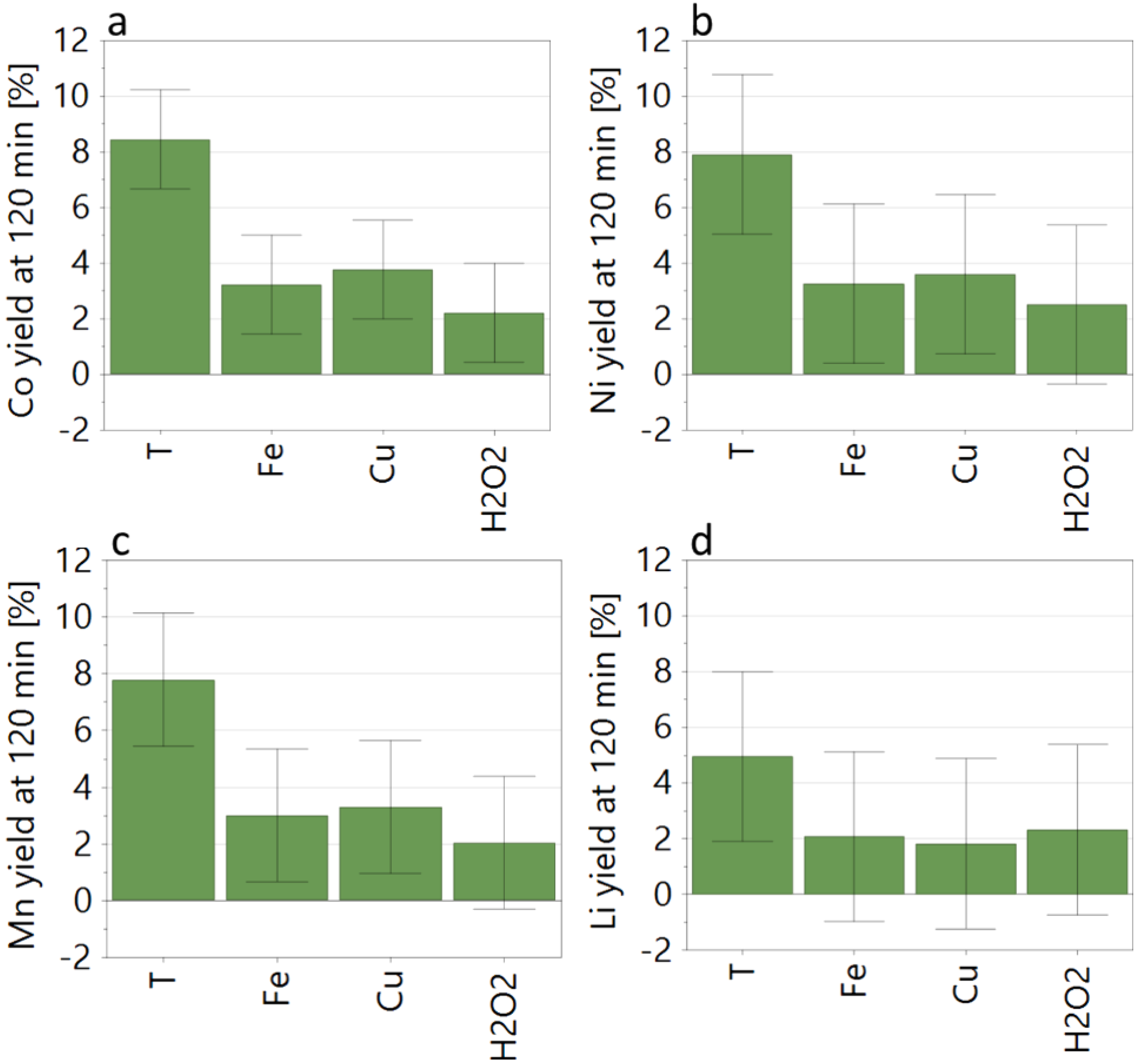
Impact of Experimental Factors on Specific Key Elements



- Temperature is the most impactful factor for all target elements
- Temperature is especially key for Li leaching yield due to increased rate of dissolution
- Addition of Cu and Fe have significant effects on final leaching yields
- Use of H_2O_2 has less impact than Fe/Cu additions on leaching
- H_2O_2 main influence on Co yield
- Predictions subject to small errors due to black mass inhomogeneity

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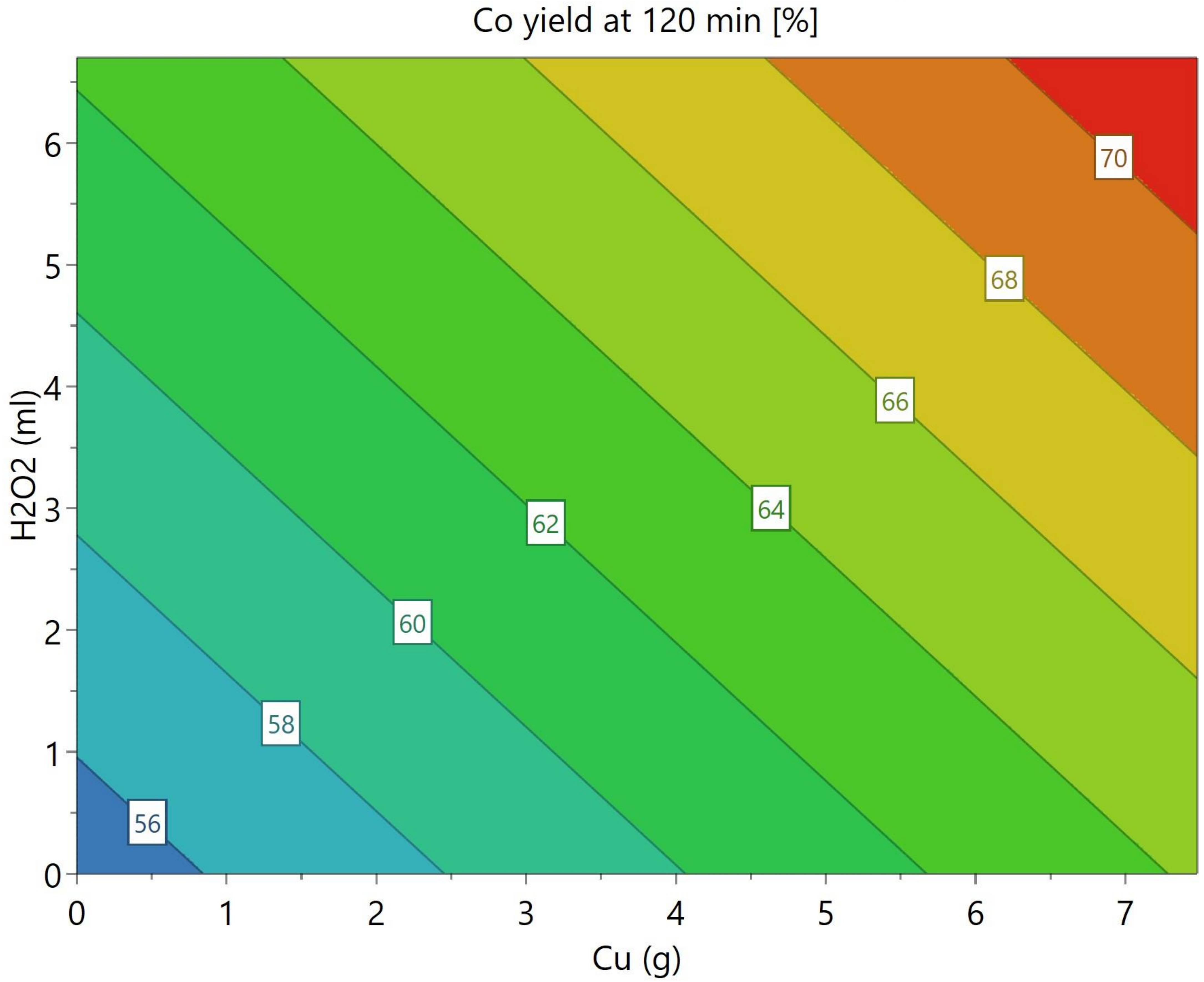
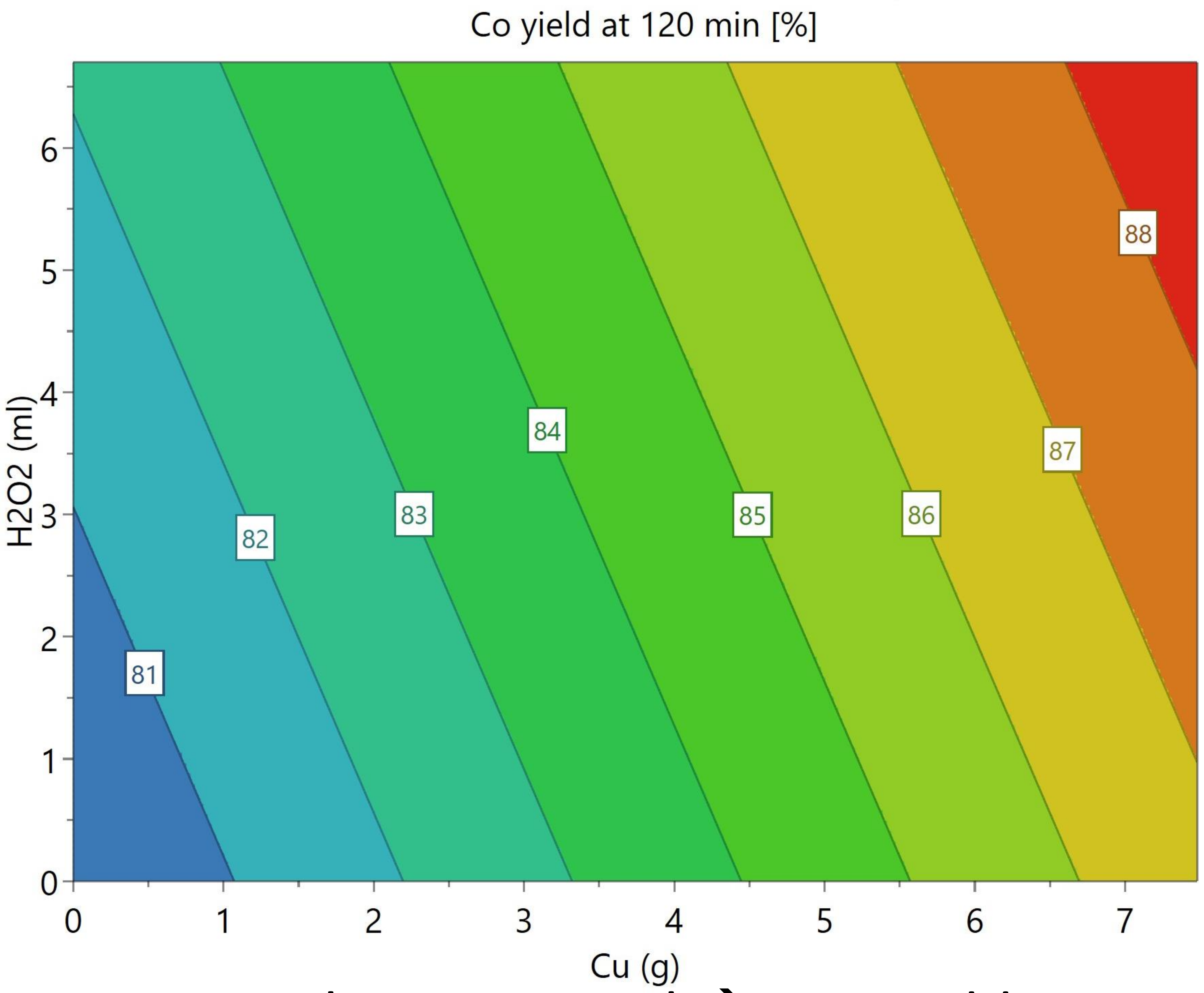
Contour plots of Co at 30 °C and 50 °C

- Cu and H_2O_2 as variables
- T=30 °C, Fe = 0.2 g/L





- Lines are almost diagonal → Cu and H_2O_2 additions have a similar impact on leaching yields

- Lines are almost vertical → H_2O_2 addition has a very weak impact on leaching yields
- Higher temperature decreases the relative efficiency of H_2O_2 as a reductant

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Conclusions

- Statistical models for Co, Ni, and Mn yields were built using T, Fe, and Cu as variables, whereas H_2O_2 addition only showed statistical validity for Co.
- Models indicated that Cu additions were more beneficial for improving cathode metal yields compared to H_2O_2.
- Demonstration that utilization metallic impurities within black masses instead preferable to use of peroxide as the reductant.
- Furthermore, these models allow for leaching performance prediction and reductant amount calculation for process design and experiment planning purposes.

$$Co\ yield(\%) = 0.90\cdot[T] + 31.4\cdot[Cu/TM] + 1800\cdot[Fe/TM] + 18.5\cdot[H_2O_2/TM] + 16.6$$

$$Ni\ yield(\%) = 0.84\cdot[T] + 30.1\cdot[Cu/TM] + 1820\cdot[Fe/TM] + 23.2 \quad (9)$$

$$Mn\ yield(\%) = 0.83\cdot[T] + 27.6\cdot[Cu/TM] + 1680\cdot[Fe/TM] + 24.6$$

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