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Extraction of Rare Earth Metals from NiMH Battery Scrap via Selective Sulfation Roasting

Jayasree Biswas[1], Esther Esekheigbe[2], Jere Partinen[2], Mari Lundström[2], Ari Jokilaakso[2]
1. Dept. of Metallurgical Engineering and Materials Science, IIT Bombay, Mumbai, India
2. Dept. of Chemical and Metallurgical Engineering, Aalto University, Espoo, Finland

1 INTRODUCTION

- Rare earth elements (REEs) have critical role in digital and clean technology transitions. However, their supply risk has become a concern (Fig 1).
- Nickel metal hydride (NiMH) battery scrap contains 10 – 20% REEs. This could be potential secondary source for REEs.
- NiMH battery market, although facing competition with Li-ion battery, is still 2.7 billion USD in 2023, which will generate significant volume of end of life batteries.

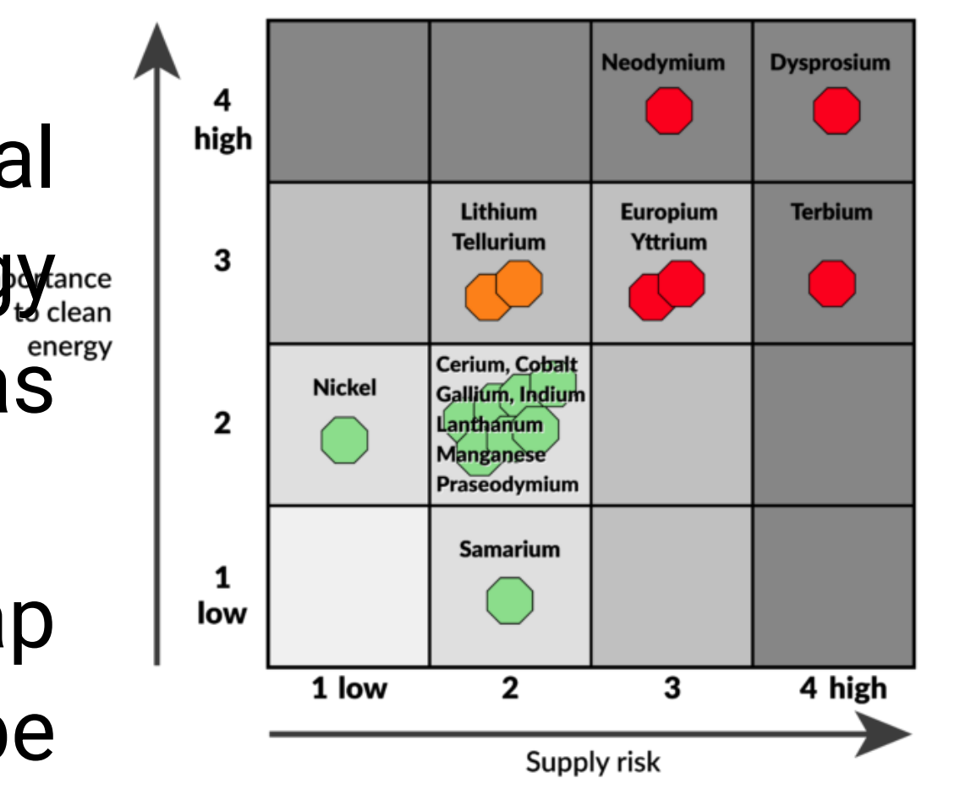


Fig 1: Importance vs supply risk of metals

Objective: Can REEs be extracted selectively from NiMH scrap?

2 MATERIALS & METHODS

Raw Materials: The NiMH scrap (<125 µm) sample composition

Ni	Co	Mn	Zn	K	Na	Fe	La	Ce	Nd	Pr	Sm	Y
39.5	5.48	2.24	1.26	1.95	0.51	0.42	10	4.8	1.7	0.59	0.35	0.17

Procedure:

Water Washing → Sulfation Roasting under SO_2, O_2, Ar gas at medium temperature → Water Leaching

The water leached solution was filtered. The leach residue was digested in aqua regia. The metal concentration in both solutions was analyzed.

Extraction efficiency (%) $= \frac{m_1}{m_1+m_2} * 100\%$, where m_1 is mass of the specific metal formed sulfates, m_2 is mass of the specific metal remaining in the residue.

3 THERMODYNAMICS

The roasting conditions were selected from stability diagram (Fig 2), varying partial pressure of SO_2 (1 – 10%), O_2 (1 – 10%) and temperature (700 °C – 850 °C).

The aim was selective formation of REE sulfates, which are water soluble, leaving other metal as oxides.

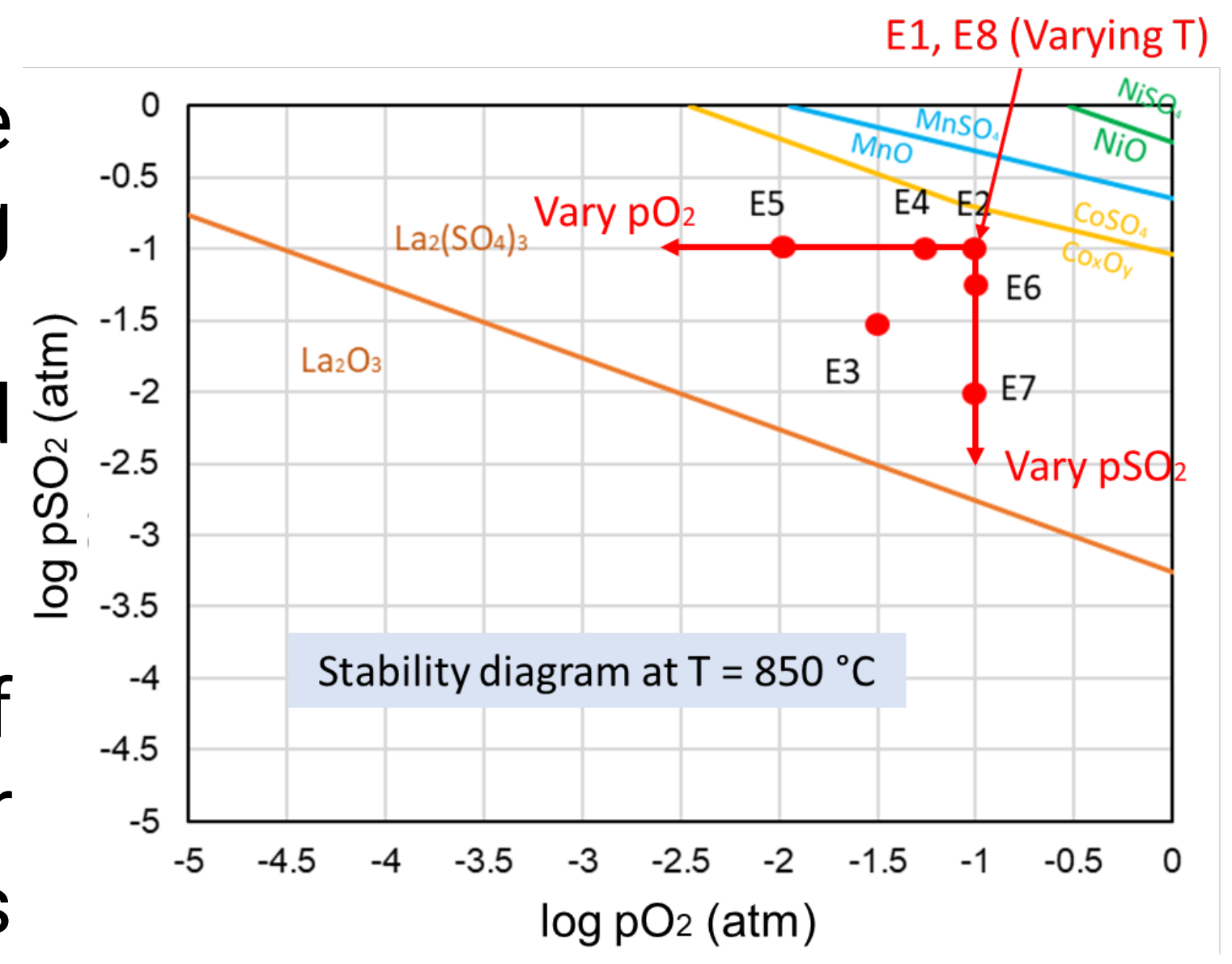


Fig 2: Metal oxide/metal sulfate stability lines at 850 °C for Ni-Co-Mn-La-S-O system using HSC software

4 RESULTS

Due to water washing, the extraction efficiency of REEs into water improved significantly (27 to 65% La) from roasted scrap. This was due to removal of Na, K from scrap.

The selective extraction of REEs was found to be best for E3 condition i.e. 3% SO_2, 3%O_2, Ar at 850 °C for 60 min; achieved extraction efficiency of 65% La, 58% Ce, 59% Pr, 58% Nd, 0.4% Ni, 4% Co.

Roasting for longer times - 1 hr, 2 hrs, 4 hrs at E3 condition did not improve the REEs extraction efficiency.

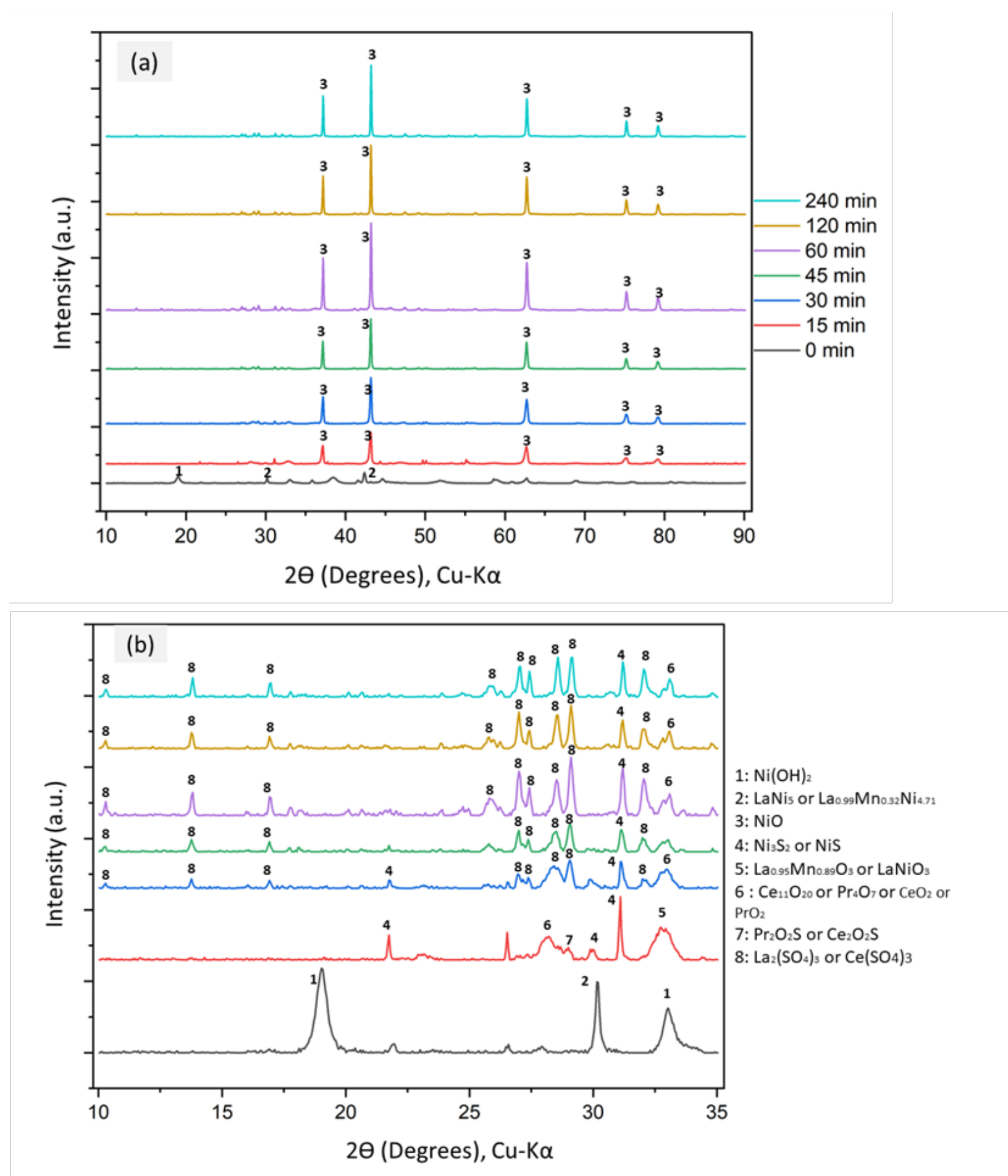
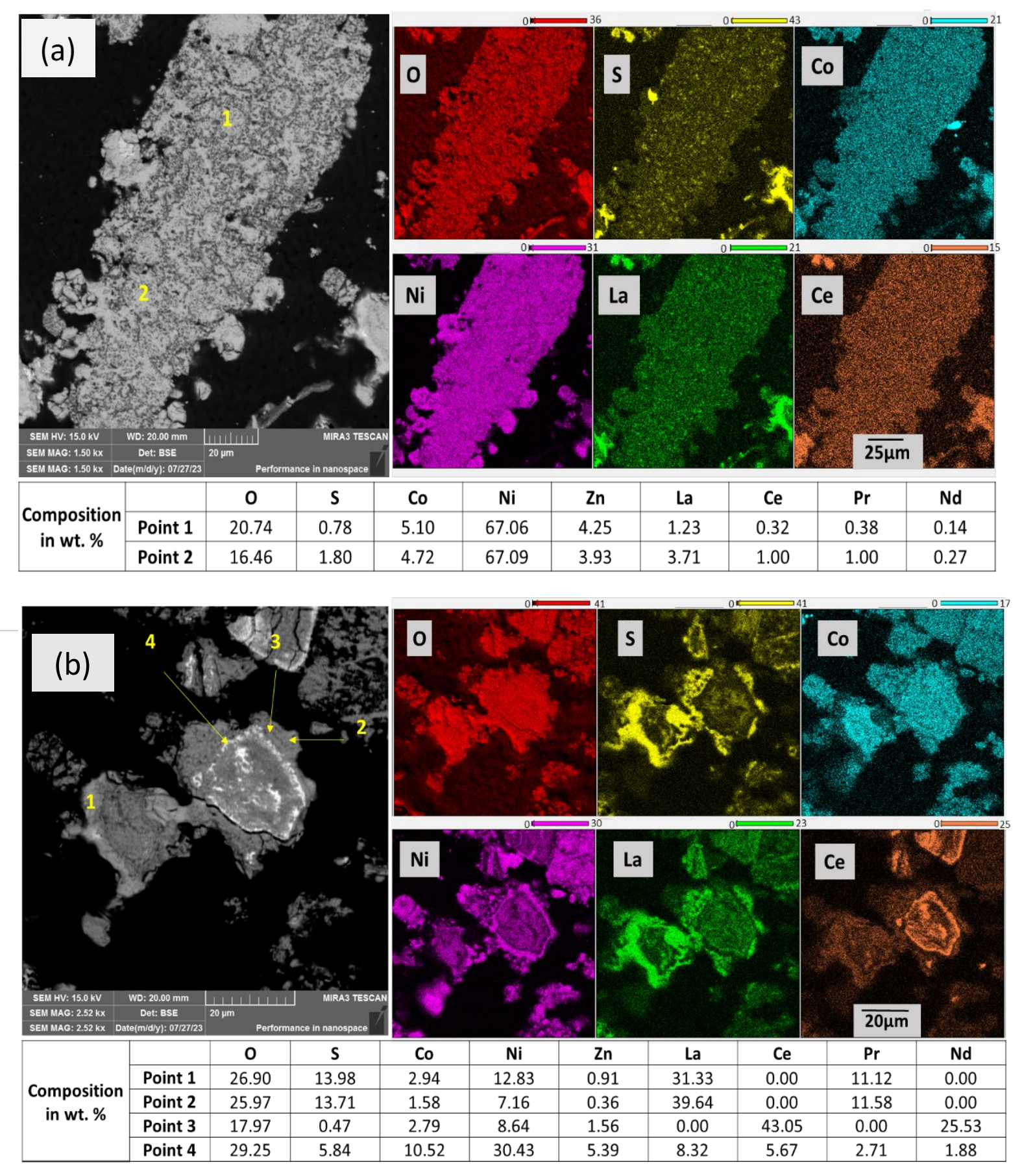


Fig 3: XRD analysis of different time roasted samples in E3 condition (a), smaller angle in (b)



Composition in wt. %		O	S	Co	Ni	Zn	La	Ce	Pr	Nd
	Point 1	20.74	0.78	5.10	67.06	4.25	1.23	0.32	0.38	0.14
	Point 2	16.46	1.80	4.72	67.09	3.93	3.71	1.00	1.00	0.27

Composition in wt. %		O	S	Co	Ni	Zn	La	Ce	Pr	Nd
	Point 1	26.90	13.98	2.94	12.83	0.91	31.33	0.00	11.12	0.00
	Point 2	25.97	13.71	1.58	7.16	0.36	39.64	0.00	11.58	0.00
	Point 3	17.97	0.47	2.79	8.64	1.56	0.00	43.05	0.00	25.53
	Point 4	29.25	5.84	10.52	30.43	5.39	8.32	5.67	2.71	1.88

Fig 4: SEM – EDS mapping of 60 mins roasted sample in E3 condition - cathode particles in (a) and anode particles in (b)

Cathode particles (Fig 4a): $Ni(OH)_2 \rightarrow NiO + H_2O$

Anode Particles (Fig 4b): $2LaNi_5 + 3SO_2 + 8O_2 \rightarrow La_2(SO_4)_3 + 10NiO$

- The REE sulfation reaction happens through sequence of stages (Fig 3) – $LaNi_5 \rightarrow LaNiO_3 \rightarrow La_2O_3 \rightarrow La_2(SO_4)_3$
- The REE sulfation reaction almost stopped after 60 mins, when the product layers (La_2O_3, $La_2(SO_4)_3$) have grown as shown in Fig 4b.

5 DISCUSSION

In the sulfation roasting of the NiMH scrap, REEs selectively formed water soluble sulfates, leaving Ni, Co as oxides as predicted from thermodynamic stability diagram. Therefore, the selective extraction of REE was possible. However, the slower transport kinetics through product layer hindered the REE sulfation reaction. A potential flowsheet for NiMH scrap processing is presented in Fig 5.

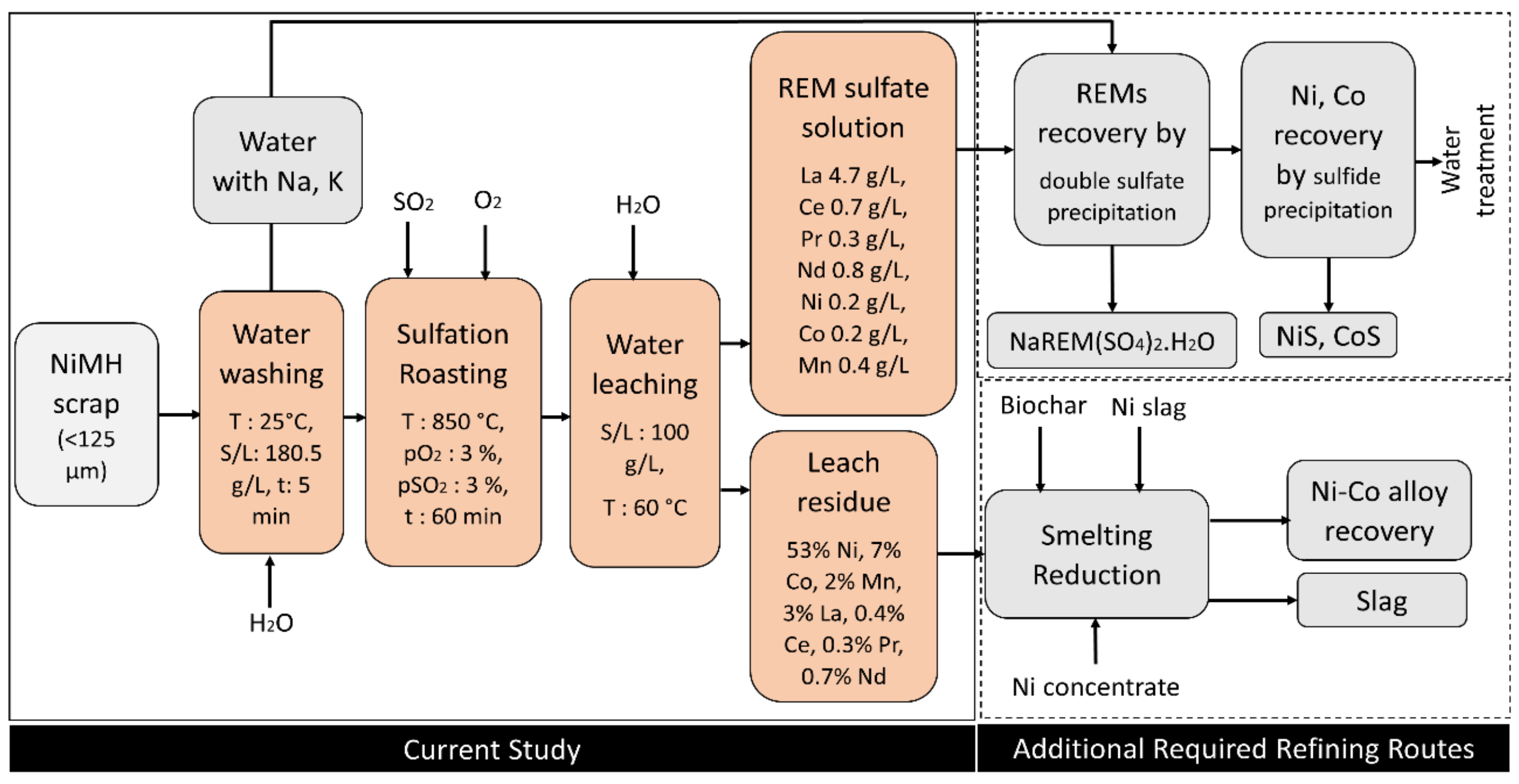


Fig 5: A potential strategy for processing NiMH battery scrap

6 CONCLUSION

- The sulfation roasting followed by water leaching route has been demonstrated to be effective in selective extraction of REEs from NiMH battery scrap.
- Roasting for longer duration did not improve the REE extraction efficiency, possibly due to slower transport kinetics of reacting species through product layer.

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