
BAUXITE RESIDUE
VALORISATION AND
BEST PRACTICES
CONFERENCE
Leuven
5-7 October 2015

Recovery of rare earth elements from Hungarian red mud with combined acid leaching and liquid-liquid extraction

Éva Ujaczki[1,2], **Yannick S Zimmermann**[1,3], **Christoph A Gasser**[1,3], **Viktória Feigl**[2] **and Markus Lenz**[1,4]

[1] Institute for Ecopreneurship, University of Applied Sciences and Arts Northwestern Switzerland, School of Life Sciences, Muttenz, Switzerland

[2] Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Budapest, Hungary

[3] Institute for Environmental Research (Biology V), RWTH Aachen University, 52074 Aachen, Germany

[4] Department of Environmental Technology, Wageningen University, Wageningen, The Netherlands

Bauxite Residue Valorisation and Best Practices Conference

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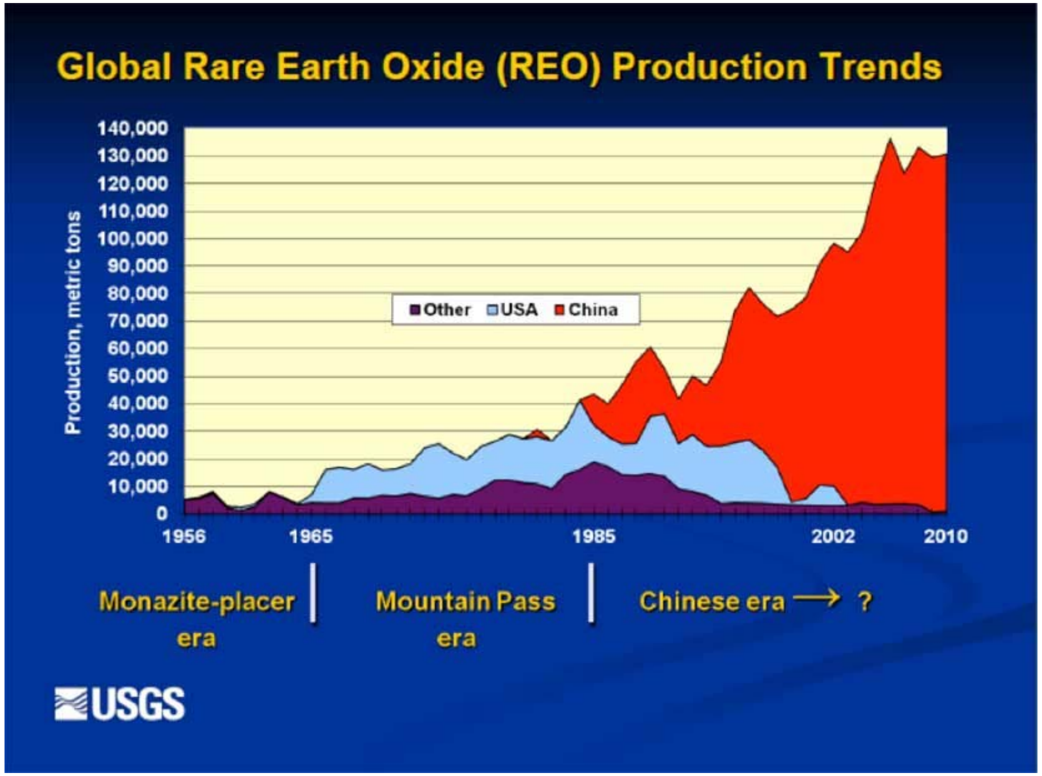
Critical raw materials

- CRM: above average economic importance and supply risk
- LCD screens, computer chips, optical media, rechargeable batteries, mobile phones, magnets and car components
- 20 CRM: abiotic + biotic; single elements + elemental groups (light + heavy REE) China controls approx. 97% of the world`s REE market → alternative sources



http://www.rareelementresources.com/rare-earth-elements#.VMI219LF98E

Red mud

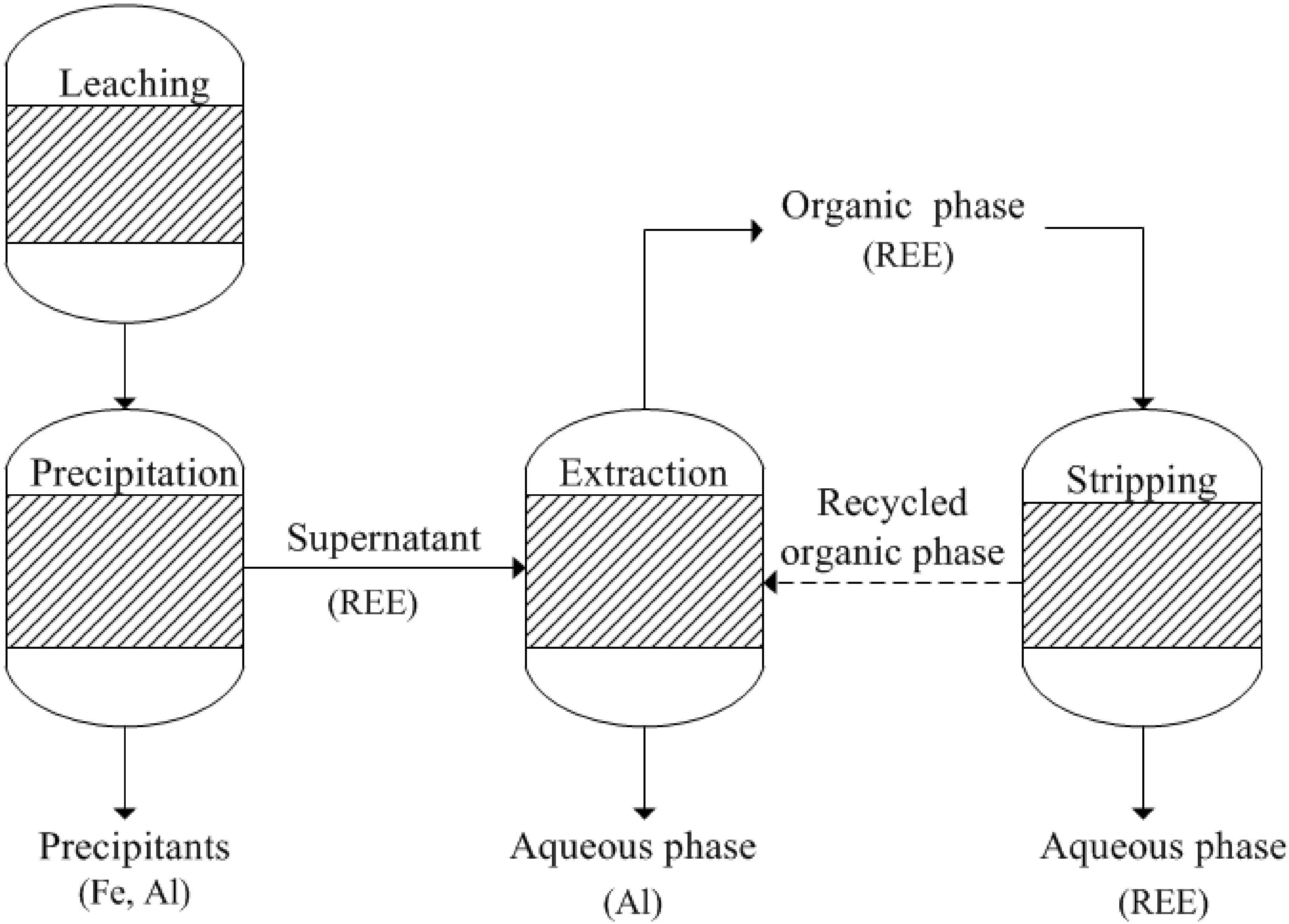
- Produced by Bayer process
- Stored after dewatering by filter presser and drying at the disposal area
- moisture content of 28%
- pH 12
- Main composition: Al, Ca, Fe, Na, Ti, Si
- total REE concentration: > 0.11 wt% (1082 mg kg^{-1})

Objectives

Evaluation of Hungarian red mud as a secondary source of critical raw materials

- CRM inventory (XRF, ICP-MS)
- Extractability: type of acid HCl, HNO_3, H_2SO_4 and $C_6H_8O_7$, $C_2H_2O_4$
  - process parameters (acid concentration, time, T, S:L)
- Purifying elements of interest from the leachate: liquid-liquid extraction
  - process parameters (complexing agent concentration in organic phase, O/A(extraction) ratio, acid concentration, O/A(stripping) ratio)

Flow scheme of the overall process combination



Rare earth composition

Element	Concentration [mg kg^{-1}]	Price* [t^{-1}]	Overall economic value [t^{-1}]	Element	Concentration [mg kg^{-1}]	Price* [t^{-1}]	Overall economic value [t^{-1}]
Sc	80.0 ± 2.6	$12,500	$1.00	**Gd**	26.6 ± 0.4	$12,500	$0.33
Y	100 ± 9	$12,500	$1.25	**Tb**	3.69 ± 0.35	$61,500	$2.27
La	166 ± 1	$5,000	$0.83	**Dy**	21.2 ± 0.1	$685,000	$14.55
Ce	430 ± 3	$4,500	$1.93	**Ho**	4.15 ± 0.06	$12,500	$0.05
Pr	39.2 ± 0.3	$12,500	$0.49	**Er**	12.0 ± 0.2	$750,000	$8.48
Nd	151 ± 1	$58,000	$8.76	**Tm**	1.78 ± 0.03	$12,500	$0.02
Sm	27.9 ± 2.4	$12,500	$0.35	**Yb**	10.8 ± 1.2	$12,500	$0.28
Eu	6.07 ± 0.01	$12,500	$0.08	**Lu**	1.72 ± 0.17	$15,500	$0.02

*Values from U.S. Geological Survey (USGS 2015)

- 1 ton red mud: max. $64.2
- $38.2 ton^{-1} of $64.2: REE

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Comparison with other red muds

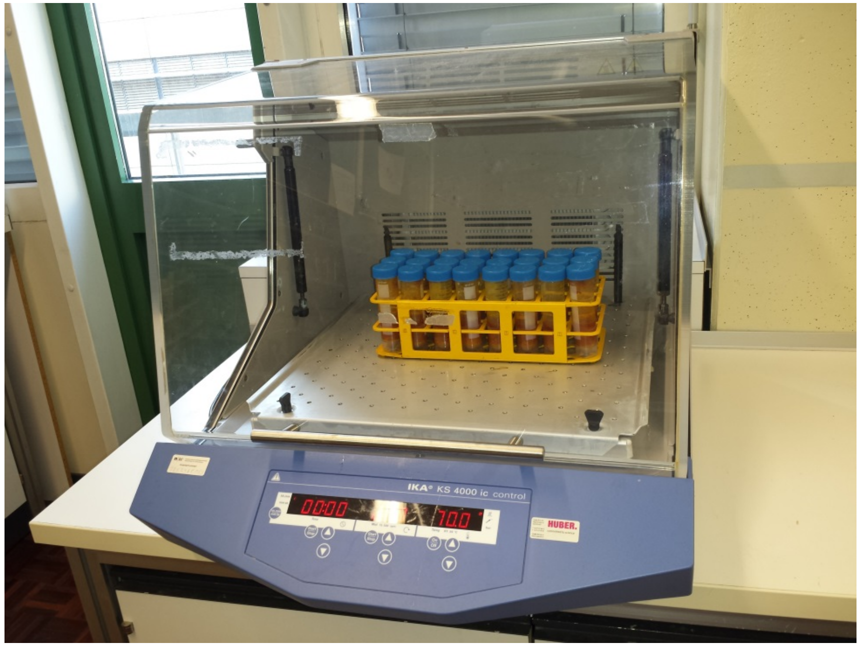
Bauxite source	Most abundant elements of the REEs Concentration [mg kg^{-1}]				Reference
	Sc	Y	Ce	La	
North Jamaica	101	760	684	1540	Rayzman 1998
Jamaica	107	485	591	1508	Rayzman 1998
Guinea	76.9	293	319	651	Rayzman 1998
Greece	121	75.7	368	114	Borra et al. 2015
Hungary	80.0	100	430	166	Ujaczki et al., 2015 under review

Borra, C.R., Pontikes, Y., Binnemans, K., Van Gerven, T. (2015) Leaching of rare earths from bauxite residue (red mud). Minerals Engineering, 76, 20-27.
Rayzman, V.L. (1998) Red mud revisited - Special paper on scandium potential, Aluminium Today10.5 ,64,68.
Ujaczki, É., Zimmermann, Y-S., Gasser, A,C., Molnár, M., Feigl, V., Lenz, M. (2015) Red mud as a secondary source of critical raw materials. Part A: Extraction. Under review.

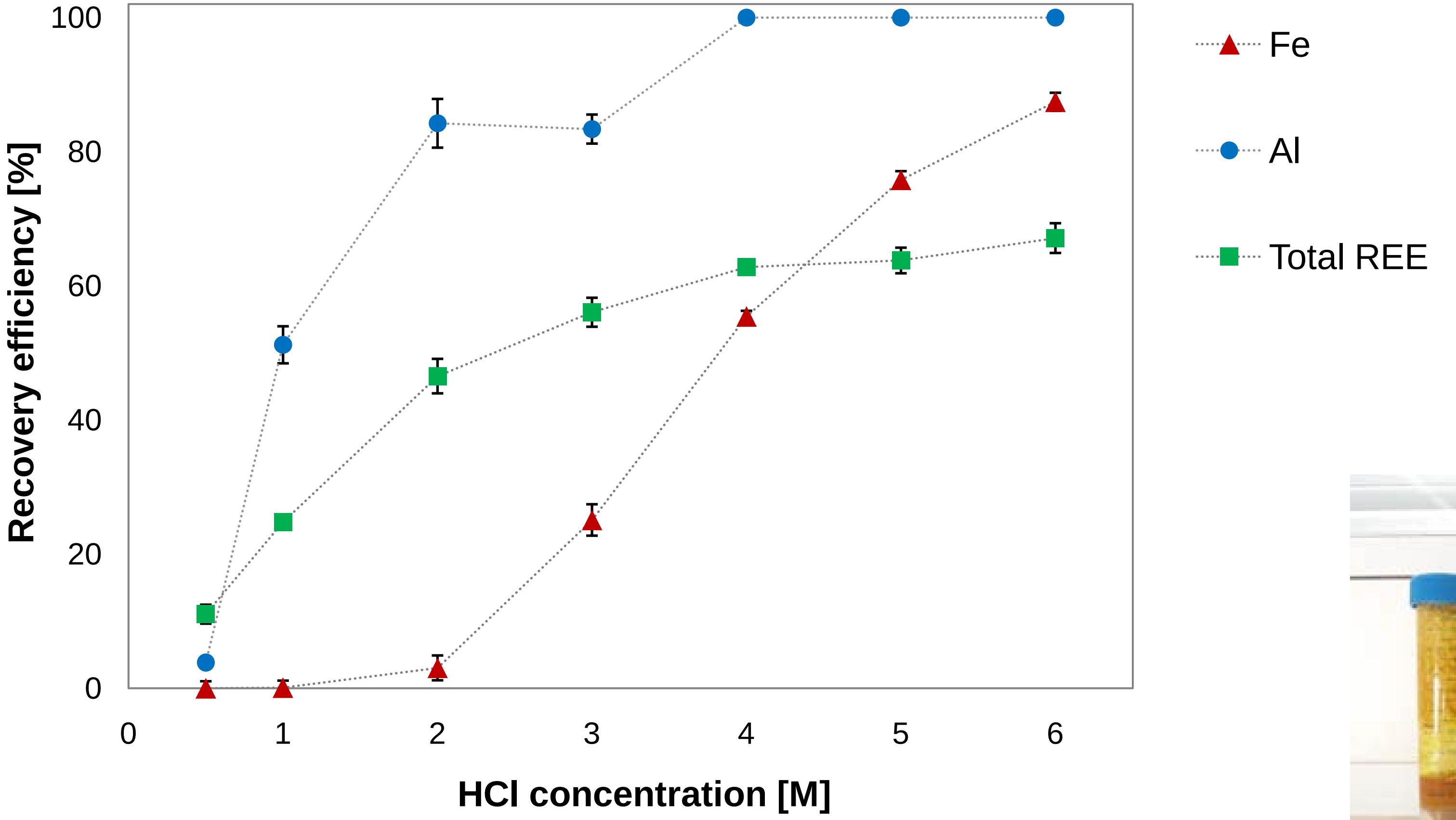
Leaching experiments

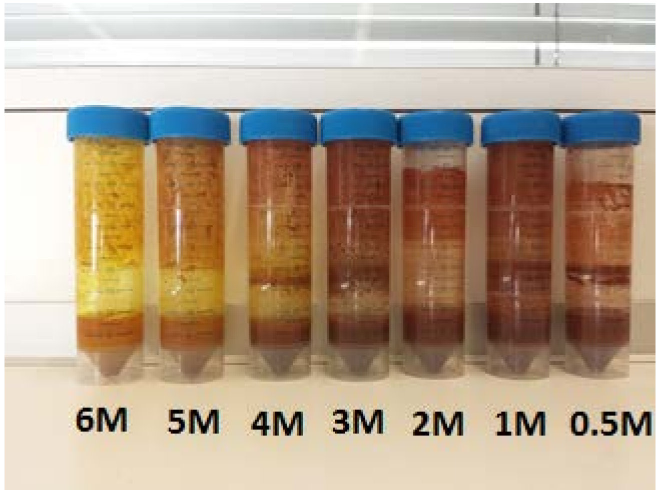
- Extractability: type of acid HCl, HNO_3, H_2SO_4 and $C_6H_8O_7$, $C_2H_2O_4$
- process parameters (concentration, time, T, S:L)

Parameters	Experimental Conditions
HCl concentration (M)	0.5–6
H_2SO_4 concentration (M)	1
HNO_3 concentration (M)	2
$C_6H_8O_7$concentration (M)	0.66
$H_2C_2O_4$ concentration (M)	1
S/L ratio (g L^{-1})	10–100
Temperature (°C)	22–90
Duration (hour)	1–24



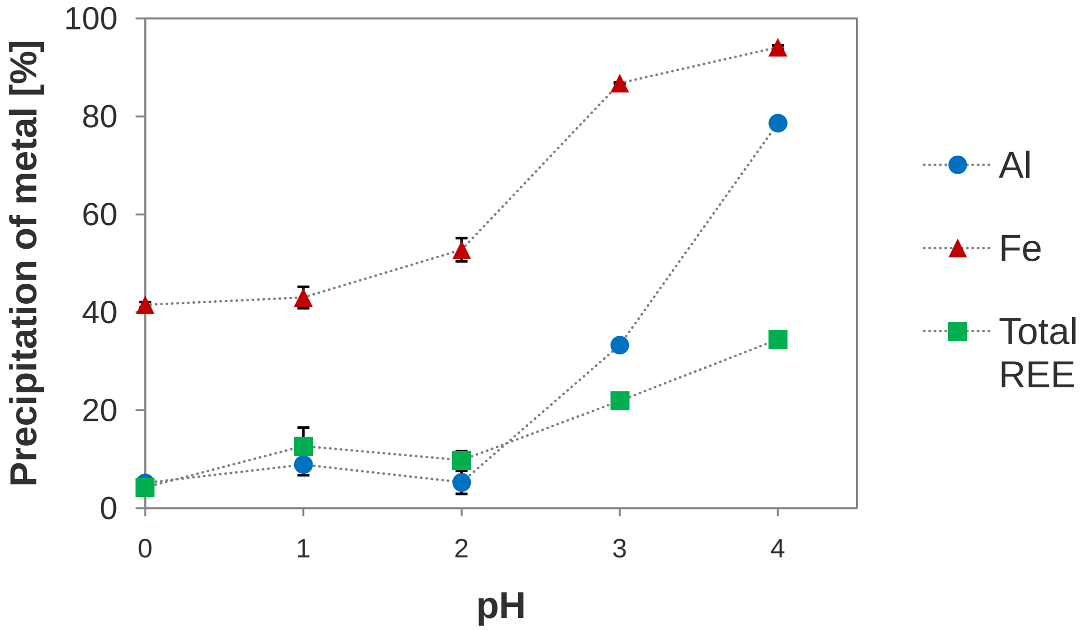
HCl concentration effect by leaching





Liquid-liquid extraction

- Al and Fe precipitation (1M NaOH)



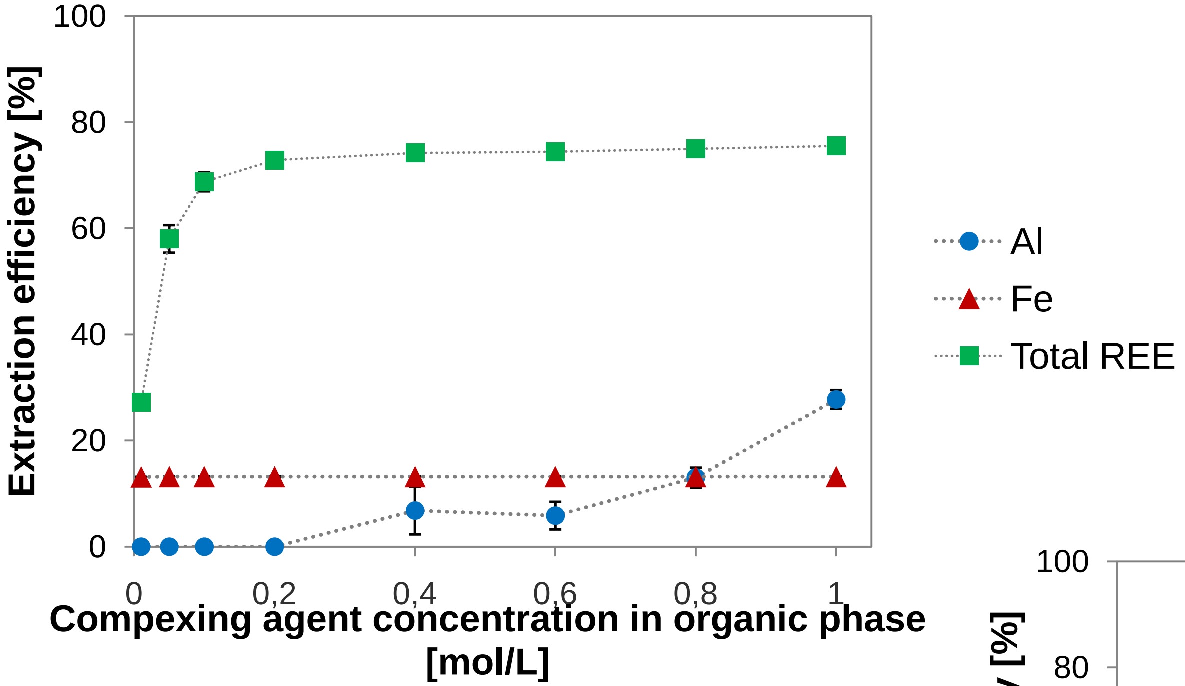
- Extraction

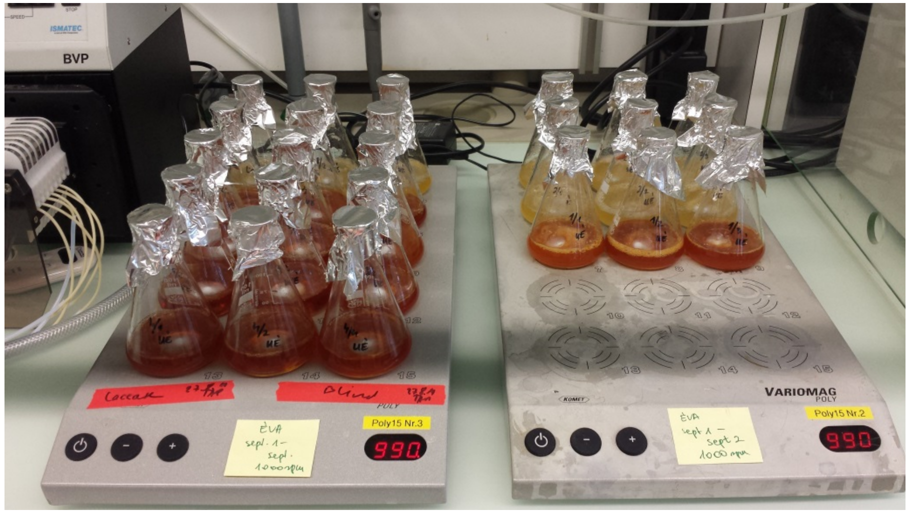
Parameters	Experimental Conditions
Complexing agent concentration (M)	0.01–1
O/A(extraction) ratio	0.1–10

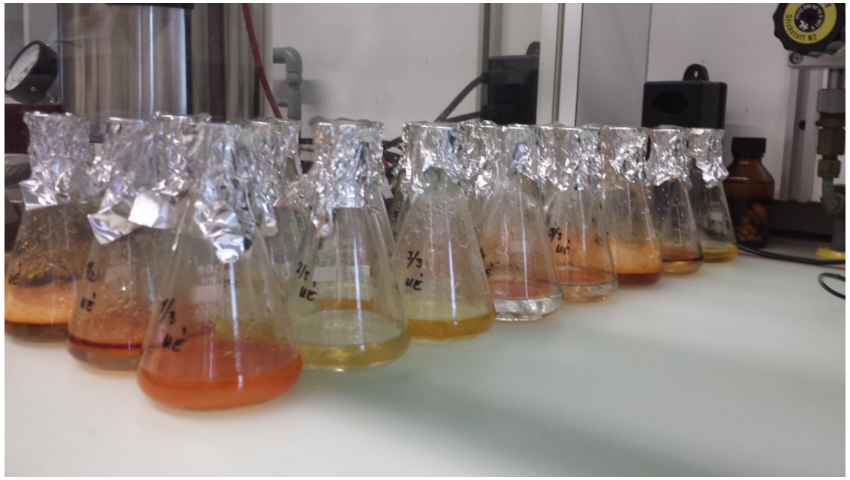
- Stripping

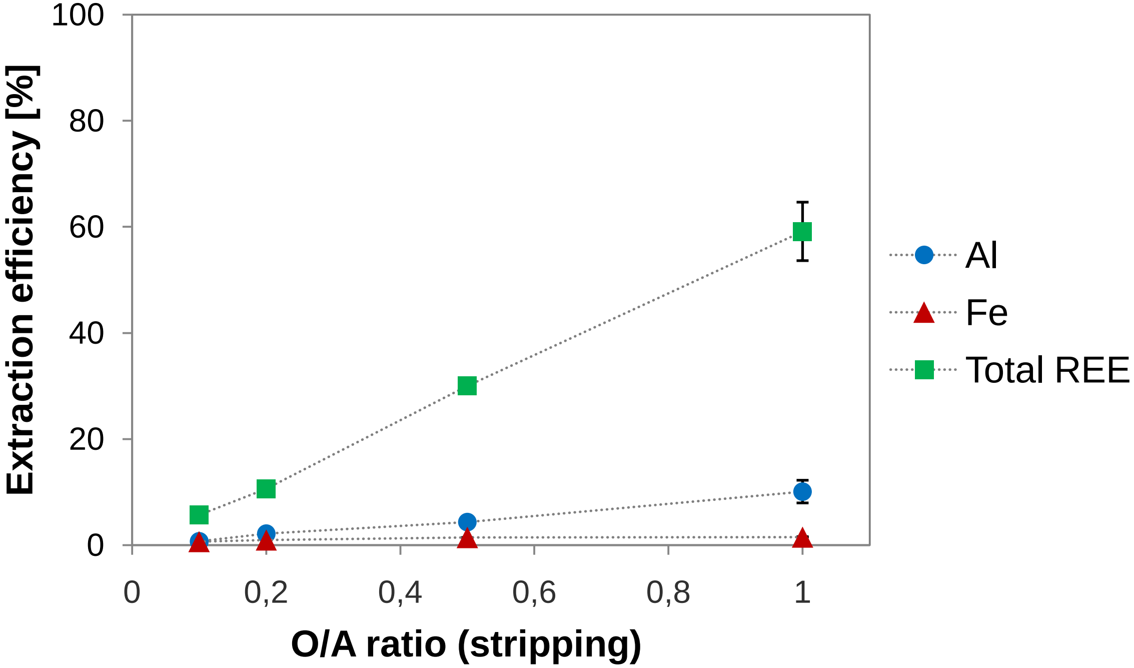
Parameters	Experimental Conditions
Acid concentration (M)	0.5–6
O/A(stripping) ratio	0.1–1

Parameters effect by LLE



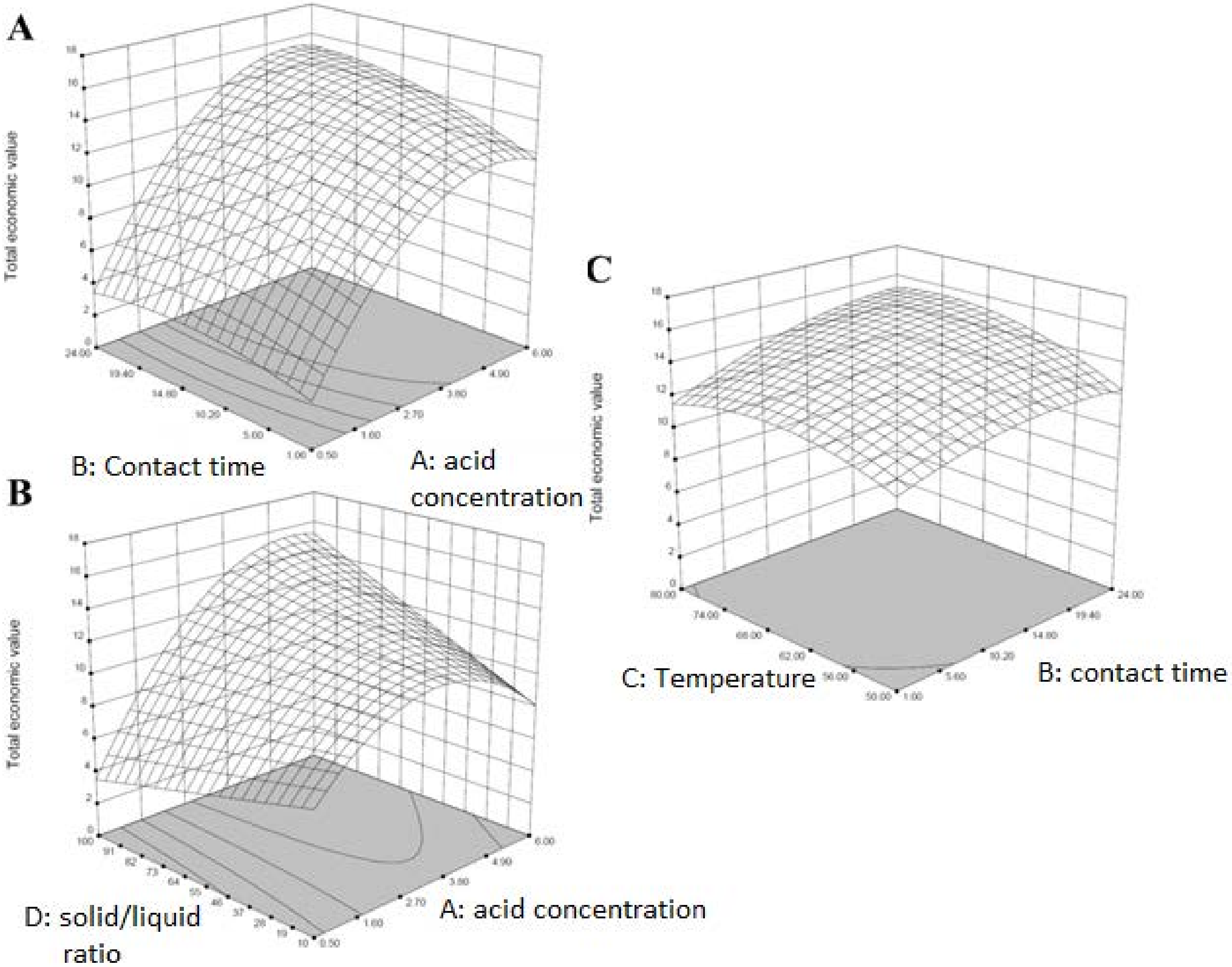






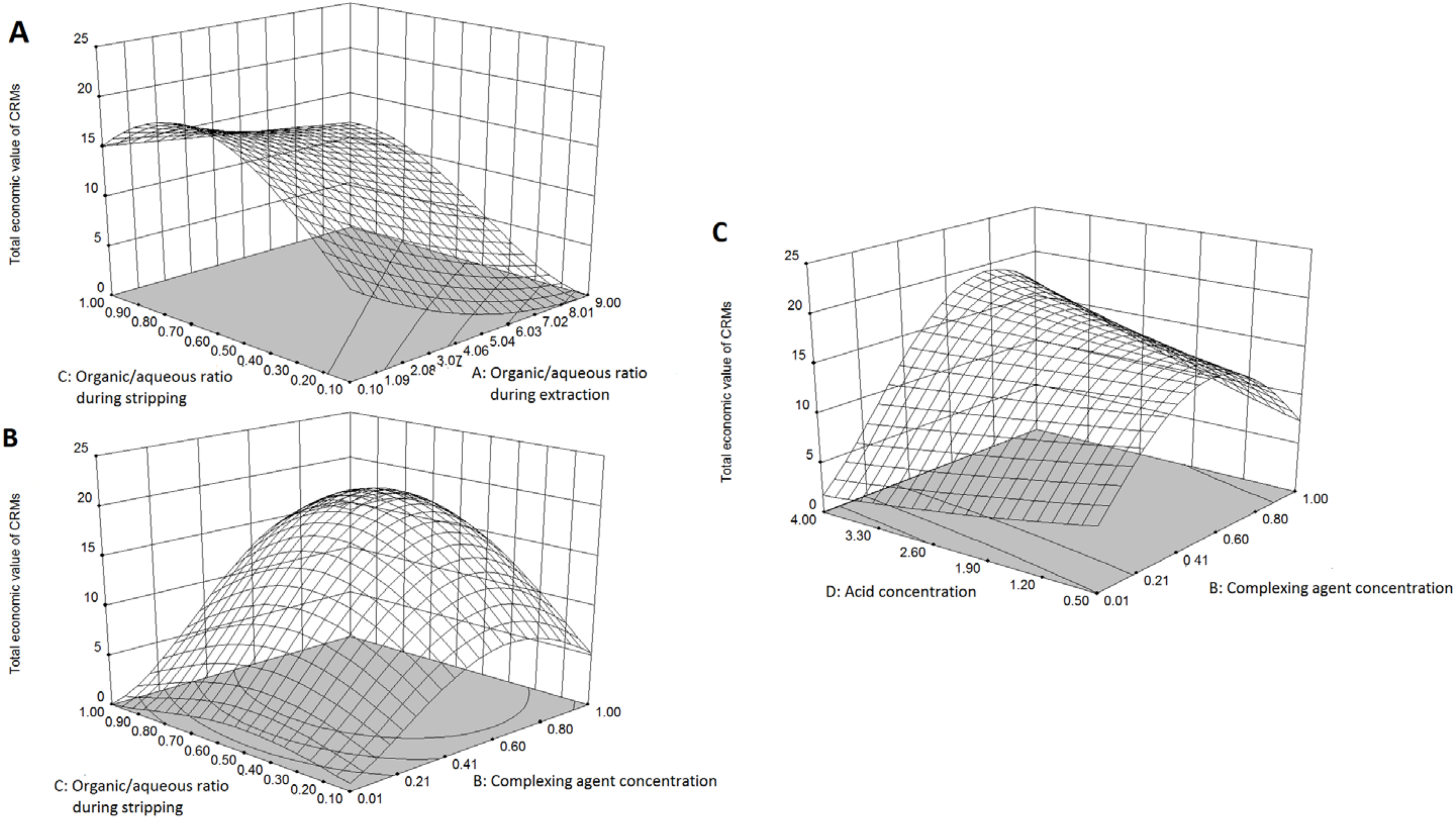
Experimental design

Element	Concentration [mg kg^{-1}]	Overall economic value [t^{-1}]
Total REEs	560	$24



Experimental design by LLE

Element	Concentration [mg kg^{-1}]	Overall economic value [t^{-1}]
Total REEs	394	$16.2



Economic perspective

Element	Recovery efficiencies [%] HCl leachate	LLE solvent	stripping media	Price [t^{-1}]	Economic value in stripping media [t^{-1}]
La	72	72	60	$4,500	$0.357
Ce	56	82	74	$12,500	$0.797
Pr	68	91	74	$58,000	$0.246
Nd	70	88	75	$12,500	$4.582
Sm	74	78	76	$12,500	$0.196
Eu	59	85	80	$12,500	$0.036
Gd	69	81	69	$615,000	$0.159
Tb	-	-	-	$685,000	$0.000
Dy	67	74	70	$12,500	$6.823
Ho	-	-	-	$705,000	$0.000
Er	61	86	57	$12,500	$2.940
Tm	-	-	-	$12,500	$0.000
Yb	66	38	24	$12,500	$0.022
Lu	-	-	-	$12,500	$0.000
Total REE					$16.2

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Interpolation

Bauxite source	Ce Concentration [mg kg^{-1}]	Ce Maximal achievable economic value with the process [t^{-1}]	La Concentration [mg kg^{-1}]	La Maximal achievable economic value with the process [t^{-1}]	Reference
Hungary	430	$0.797	166	$0.357	Ujaczki et al., 2015 under review
North Jamaica	684	$1.268	1540	$3.312	Rayzman 1998

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Summary

- Potentially valuable resource of CRM, depending on the origin
- Leaching: 62% total REE of aquaregia accessible → \$24 ton^{-1}
- Liquid-liquid extraction: 70% total REE of HCl leachable → \$16 ton^{-1}
- Future: making the proposed processes even more economically attractive
- Green alternative: leaching with citric acid needs further research
- Soil amelioration combined with metal recovery may represent a viable approach for red mud management in the future

Acknowledgement

- The financial support by Sciex-NMS^{ch} 14.044 is greatly appreciated to the recovery study .
- The study has been accomplished in the framework of the "BME R+D+I project”, supported by the grant TÁMOP 4.2.1/B-09/1/KMR-2010-0002 and was funded by a scholarship from the TÁMOP 4.2.4.A-1 project financed by the Hungarian State and the European Union and co-financed by the European Social Fund.

Research Group of Environmental Microbiology and Biotechnology at Budapest University of Technology and Economics

Institute for Ecopreneurship at University of Applied Sciences and Arts Northwestern Switzerland

Thank you very much for your attention!