HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

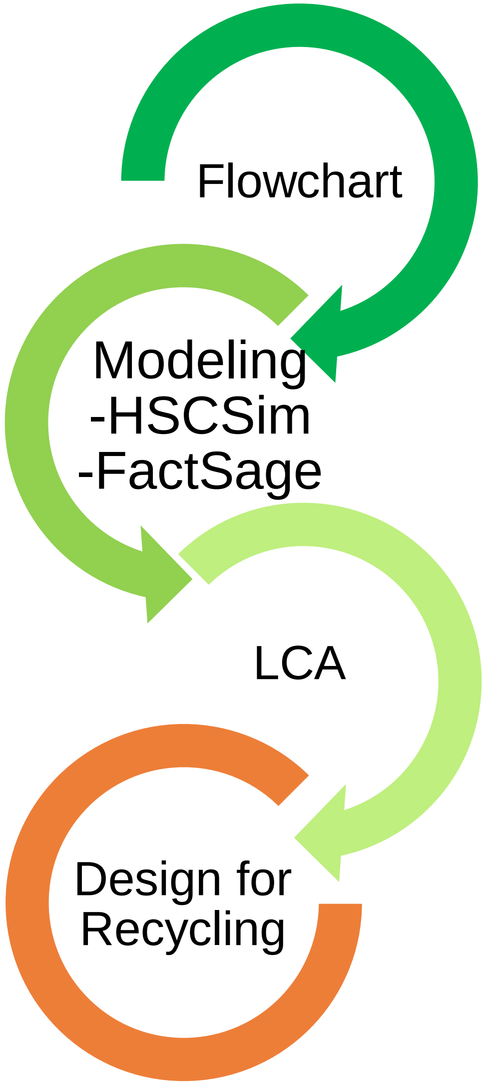
HELMHOLTZ INSTITUTE FREIBERG FOR RESOURCE TECHNOLOGY

HydroLIBRec
Optimierte Prozessketten für hydromechanisches Li-Ionen-Batterie-Recycling – HydroLIBRec

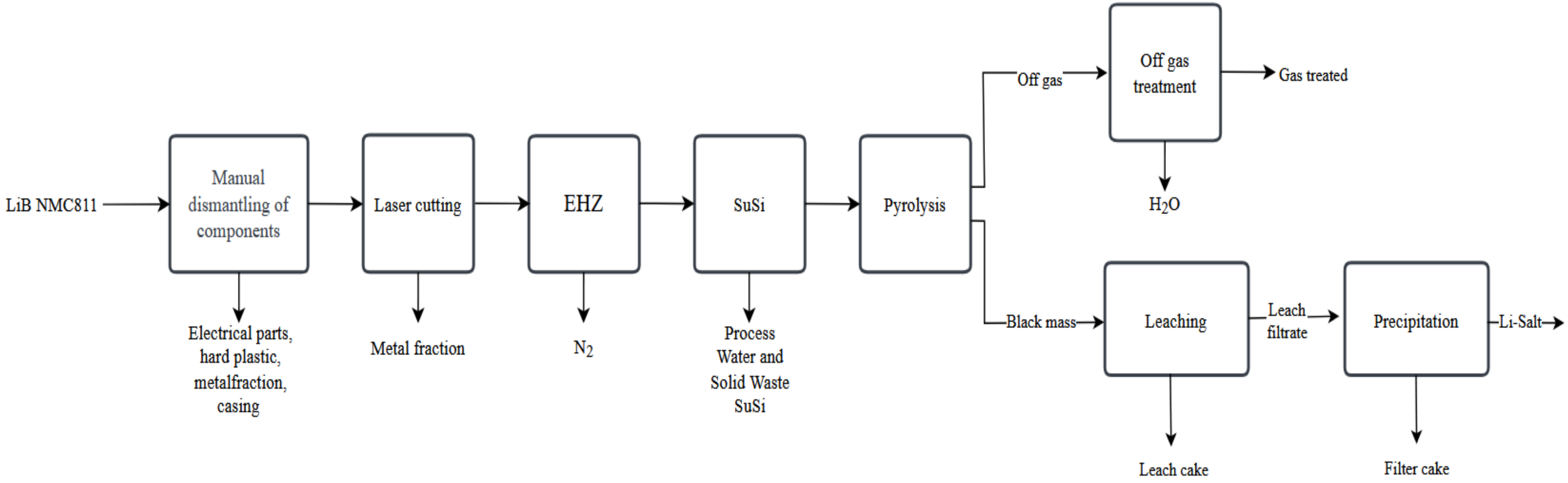
Material Flow Analysis

Modelling and Evaluation FWGB · Felipe Garcia Paz · f.garcia-paz@hzdr.de · www.hzdr.de/hif

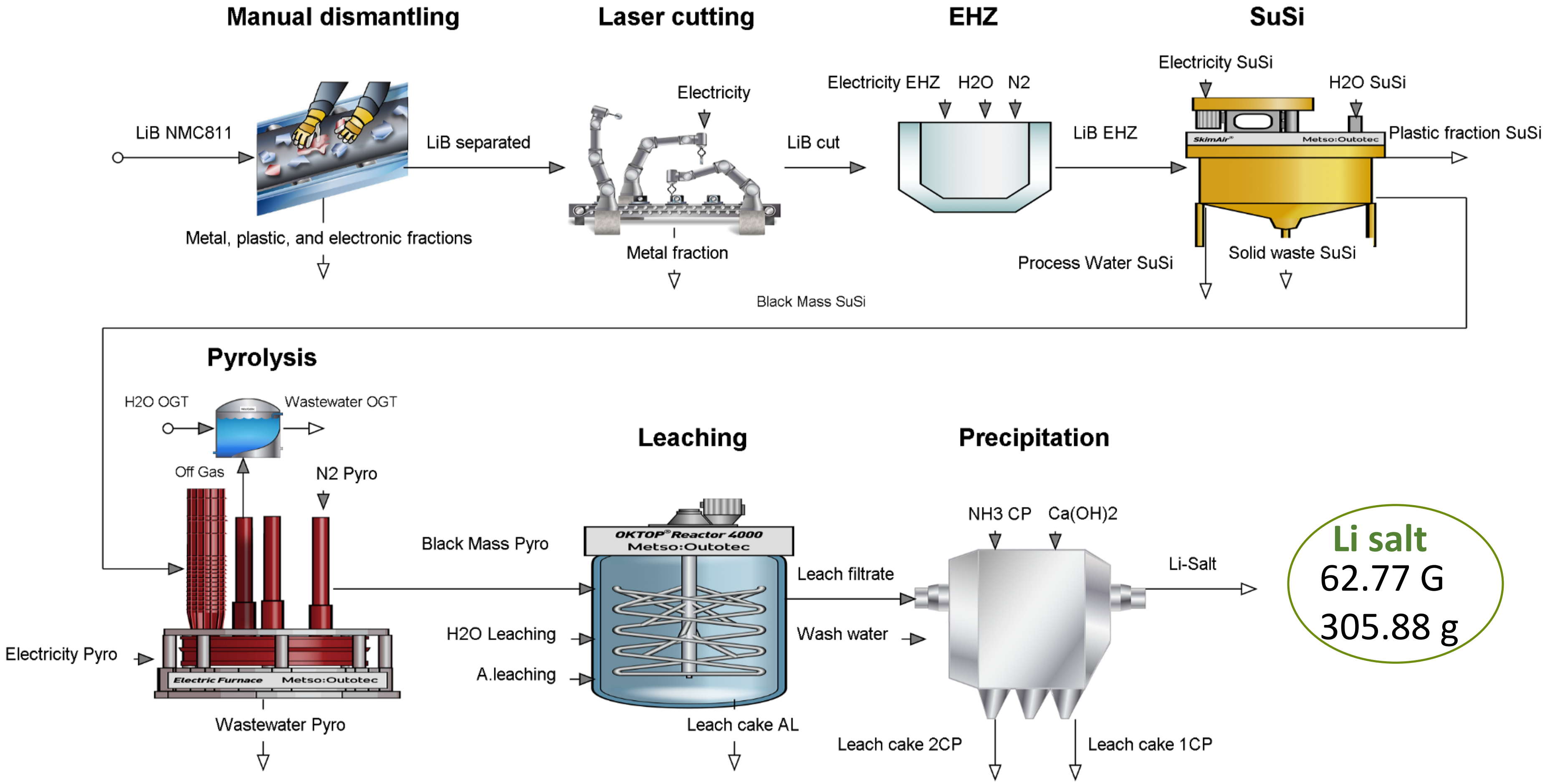
Methodology



Block flow diagram HydroLiBRec

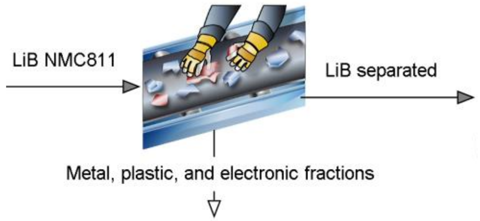


HSC Simulation Flowsheet



lithium-ion battery NMC811

Manual dismantling

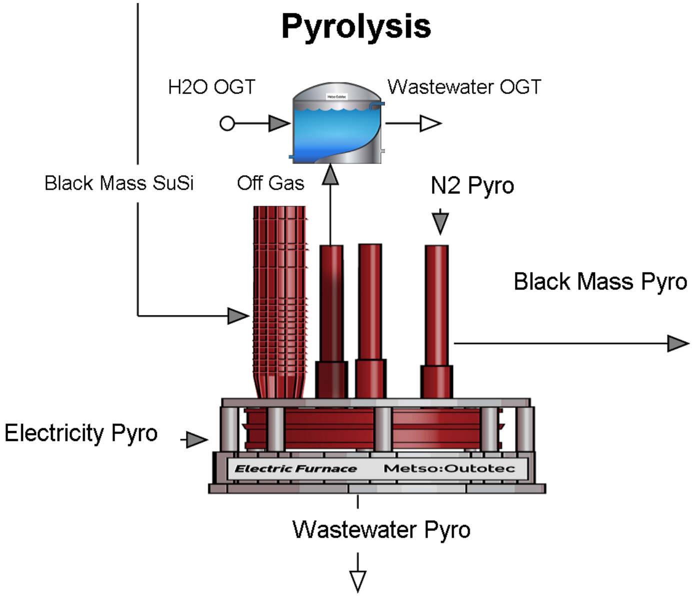


Cell Component	Composition	[wt%]
Anode	Cu	7.7%
	C	23.2%
Cathode	Al	5.0%
	NMC 811	39.8%
	Binder	2.5%
Case	Steel	15.5%
Separator foil	Polyethylene	3.3%
Elektrolyt	org. Carbonate	3.1%
Total		100.0%

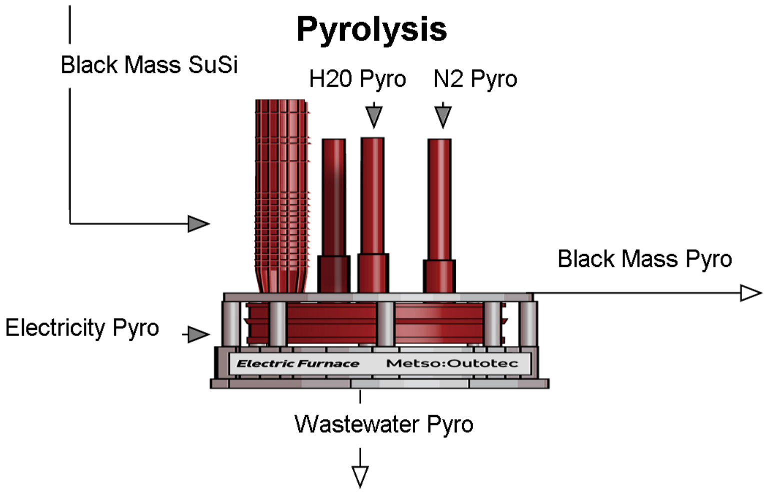
Cell Component	Composition	[wt%]
Anode	Cu	7.73%
	C	23.19%
Cathode	Al	4.97%
	Li	2.84%
	Ni	19.19%
	Mn	2.25%
	Co	2.41%
	O	13.08%
Difluoroethylene	C2H2F2	2.48%
Case	Fe	10.05%
	Ni	5.41%
Polyethylene	C2H4	3.31%
Lithium hexafluorophosphate	LiPF6	1.55%
Ethylene carbonate	C3H4O3	0.39%
Propylene carbonate	C4H6O3	0.39%
Dimethyl carbonate	C3H6O3	0.39%
Diethyl carbonate	C5H10O3	0.39%
Total		100%

lithium-ion battery NMC811

Cell Component		Composition	kg	wt%
Anode		Cu	0.0700	10.937%
		C	0.0798	12.475%
Cathode		Al	0.0497	7.765%
		NMC 811		0.000%
		Li	0.0250	3.913%
		Ni	0.1694	26.471%
		Mn	0.0198	3.097%
		Co	0.0213	3.322%
		O	0.1155	18.040%
Anode		Binder		0.000%
PVDF	fluoropolymer	C2H2F2	0.0300	4.687%
Case		Steel		0.000%
		Fe	0.0168	2.625%
		Ni	0.0091	1.416%
Extra element	OffGas	Br	0.0000001	0.00002%
	Black Mass	B	0.0001	0.017%
	OffGas	Cl	0.0000005	0.00008%
	Black Mass	S	0.0006	0.097%
	Black Mass	Ca	0.0013	0.201%
	Blck Mass	Mg	0.0002	0.037%
	Black Mass	Na	0.00004	0.006%
	Blck Mass	Si	0.0032	0.504%
Elektrolyt, org. Carbonate	lithium hexafluorophosphate	LiPF6	0.0281	4.388%
Total			0.6400	100%



ICP-OES to XRD



- The carbon present in the samples triggers a carbothermic reduction of metal oxides through the gaseous intermediate CO
- The organic compounds and the graphite are oxidized by oxygen from the active material and provide the reductive atmosphere

Composition	[wt%]
Al	2.581
B	0.011
Ca	0.129
Co	3.922
Cu	3.674
Fe	1.453
Li	3.719
Mg	0.024
Mn	1.42
Na	0.004
Ni	32.633
P	0
S	0.062
Si	0.323
Insoluble (wt%)	36.339
Total (wt%)	86.293

- Metal Concentrations in Solid Samples

Composition	[wt%]
Lithium Nickel Manganese Cobalt Oxide ($Li_1Ni_{0.75}Mn_{0.1}Co_{0.15}O_2$)	27
Copper (Cu)	3
Zabuyelite (Li_2CO_3)	8
Paramelaconite (Cu_4O_3)	1
Nickel Oxide (NiO)	6
Nickel (Ni)	7
Graphite 3R (C)	49

- Transition metal oxides PXRD

ICP-OES - PXRD - FactSage

- Metal Concentrations in Solid Samples ICP-OES

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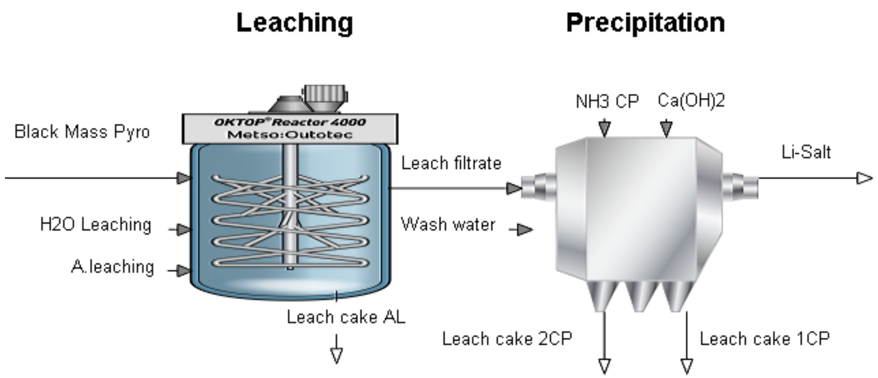
- Molecular weight calculation FactSage

Liquid	wt%	Monoxide	wt%	Solids	wt%
Al	4.81E-20	FeO	24.49	Ni_fcc	30.10
B	3.33E-15	Fe2O3	0.37	C_graphite	18.73
C	1.8368	CaO	0.0053	Cu_fcc	12.26
Ca	6.77E-22	MgO	0.059	LiAlO2	9.55
Co	18.856	Al2O3	0.084	LiF	9.48
Cu	0.25114	NiO	0.008	LiAl5O8	9.38
Fe	35.89	CoO	0.295	Li3PO4	3.88
H	7.36E-06	MnO	74.52	Co_fcc	2.88
Li	3.78E-15	CuO	2.4E-06	Li2SiO3	1.86
Mg	1.39E-16	Na2O	3.17E-15	CaMg2Al16O27	0.66
Mn	0.000128	Li2O	3.79E-07	Cu2S	0.53
N	9.1E-05	LiAlO2	0.15819	Al2O3	0.23
Na	2.7E-22			CaF2	0.23
Ni	43.166			Na2Ca3Al16O28	0.16
O	1.54E-07				
P	3.46E-12				
Si	9.3E-15				
Total	100		100		100

Leaching feed composition

Pyrolysis Output-Black Mass		
Composition	**Kg**	**[wt%]**
Al2O3	0.0157	2.58
B	0.0001	0.02
C	0.2432	39.92
CaO	0.0008	0.13
Co	0.0841	13.80
CoO	0.0253	4.15
Cu	0.0197	3.23
Cu4O3	0.0022	0.36
Cu2S	0.0004	0.07
Fe	0.0054	0.89
FeO	0.0036	0.59
Li2CO3	0.0213	3.50
LiF	0.0039	0.64
LiAlO2	0.0013	0.21
Li2SiO3	0.0013	0.21
MgO	0.0002	0.03
MnO	0.0272	4.46
Na2O	0.00005	0.01
Ni	0.1446	23.73
NiO	0.0076	1.25
Li3PO4	0.0013	0.21
Total	0.609	100
Off-Gas	4.911	



- Fraunhofer Data

lithium solution/filtrate	contains the other species as well	Output Product	0.465 l	2.266 l
filter cake 1	hazardous waste for incineration	Output Waste	172.995 g	842.988 g
Nickel Formate Hydrate Ni(HCOO)2(H2O)2			*60.548 g*	*295.046 g*
Carbon C			*46.709 g*	*227.607 g*
Cobalt Formate Hydrate Co(HCOO)2(H2O)2	*filter cake1 composition*		*53.628 g*	*261.326 g*
Cobalt Oxide CoO1.84			*5.190 g*	*25.290 g*
Manganese Hydroxide Oxide Mn(OH)O			*6.920 g*	*33.720 g*
water, deionised		Input Resource	0.563 kg	2.743 kg
formic acid		Input Product	24.626 g	120.000 g
electricity, medium voltage		Input Product	0.010 kWh	0.020 kWh
BM, pyrolyzed		**Input Product**	0.125 kg	0.609 kg

Control HSC Sim Hydro-Unit

Set of Chemical reactions happens during the Precipitation	Reactant Name	Product Output name
$Al(CHOO)_3(a)$ =3 HCOO(-a) + Al(+3a)	Aluminium triformate	Formate + Aluminium
$Fe(CHO_2)_2(a)$ =2 HCOO(-a) + Fe(+2a)	Iron(II)formate	Formate + Iron(II)
$Mg(CHO_2)_2(a)$ =2 HCOO(-a) + Mg(+2a)	Magnesium formate	Formate + Magnesium
$Ni(CHO_2)_2(a)$ =2 HCOO(-a) + Ni(+2a)	Nickel formate	Formate + Nickel
$Co(CHO_2)_2(a)$ =2 HCOO(-a) + Co(+2a)	Cobalt(II) formate	Formate + Cobalt
$Mn(CHO_2)_2(a)$ =2 HCOO(-a) + Mn(+2a)	Manganese formate	Formate + Manganese
$Cu(CHO_2)_2(a)$ =2 HCOO(-a) + Cu(+2a)	Copper(II) formate	Formate + Copper
$NaCHO_2(a)$ =Na(+a) + HCOO(-a)	Sodium formate	Formate + Sodium
2 Co + 6 HF(a) =2 CoF_3 + 3 $H_2(g)$	Cobalt + Hydrogen fluoride	Cobalt(III) Fluoride+ Hydrogen
$Ca(OH)_2$ + $CO_2(g)$ =$CaCO_3$ + H_2O	Calcium hydroxide + Carbon Dioxide	Calcium Carbonate +Water
HCOO(-a) =$CO_2(g)$ + H(+a)	Formate	Carbon Dioxide + Hydrogen
2 H_2O + 2 $CO_2(g)$ =$CH_3COOH(a)$ + 2 $O_2(g)$	Water + Carbon Dioxide	Acetic acid + Oxygen
$CaCO_3$ + Ni(+2a) =$NiCO_3$ + Ca(+2a)	Calcium Carbonate + Nickel	Nickel Carbonate + Calcium
$NiCO_3$ + 2 $CH_3COOH(a)$ + 3 H_2O =$C_4H_{14}NiO_8$ + $CO_2(g)$	Nickel Carbonate + Acetic Acid + Water	Nickel Acetate Hydrate - Carbon Dioxide
$Ca(OH)_2$ + $H_3PO_4(a)$ =$CaHPO_4$ + 2 H_2O	Calcium Hydroxide + Phosphoric Acid	Dicalcium Phosphate + Water
$NH_3(l)$ + H_2O =$NH_4(+a)$ + OH(-a)	Ammonia + Water	Ammonium + Hydroxide
Al(+3a) + 3 OH(-a) =$Al(OH)_3$	Aluminium + Hydroxide	Aluminium Hydroxide
3 $Al(OH)_3$ + 2 $H_3PO_4(a)$ =$Al_3(PO_4)_2(OH)_3*5H_2O$ + H_2O	Aluminium Hydroxide	Aluminium Phosphate Hydroxide Hydrate + Water
2 OH(-a) + Mn(+2a) =$Mn(OH)_2$	Hydroxide + Manganese	Manganese(II) Hydroxide
2 $Al(OH)_3$ + 2 $H_3PO_4(a)$ + $Mn(OH)_2$ =$MnAl_2(PO_4)_2(OH)_2*6H_2O$	Aluminium Hydroxide + Phosphoric acid + Manganese(II) Hydroxide	Manganese Aluminium Phosphate Hydroxide Hydrate
2 Na(+a) + $CaCO_3$ =Na_2CO_3 + Ca(+2a)	Sodium + Calcium Carbonate	Sodium Carbonate+ Calcium
Fe(+2a) + 2 OH = FeO + H_2O	Iron(II) + hydroxide	Iron Oxide + Water

Li IN	Li OUT
4.63 g	8.39 g
22.64 g	40.88 g

HiF

Design for Recycling- Material and product-centric recycling

Chapter 5 - Material and product-centric recycling: design for recycling rules and digital methods

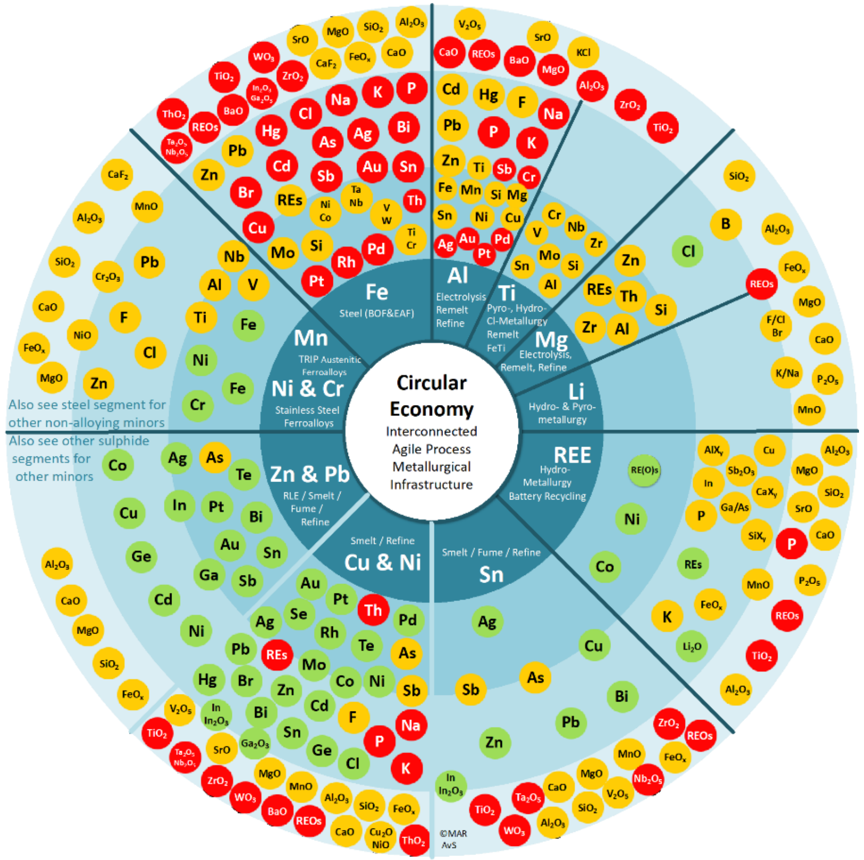
Rules and Guidelines:

1) Product-specific and recycling system-specific
2) Model and simulation quantification
3) Data in a consistent format
4) Economically viable technology
5) Computer aided design
6) Identify and minimize the use of materials that will cause losses and contamination
7) Identify components/ clusters in a product that will cause problems and losses in recycling (metal wheel)
8) Design cluster or subunits in products that can be easily removed and that match with the final treatment
9) Label, including carefully considered standardization products/components based on recovery and/or incompability.

Reuter, Markus A., and Antoinette van Schaik. "Material and product-centric recycling: design for recycling rules and digital methods." *Handbook of Recycling*. Elsevier, 2024. 79-95.

Design for Recycling- Ecodesign Strategy

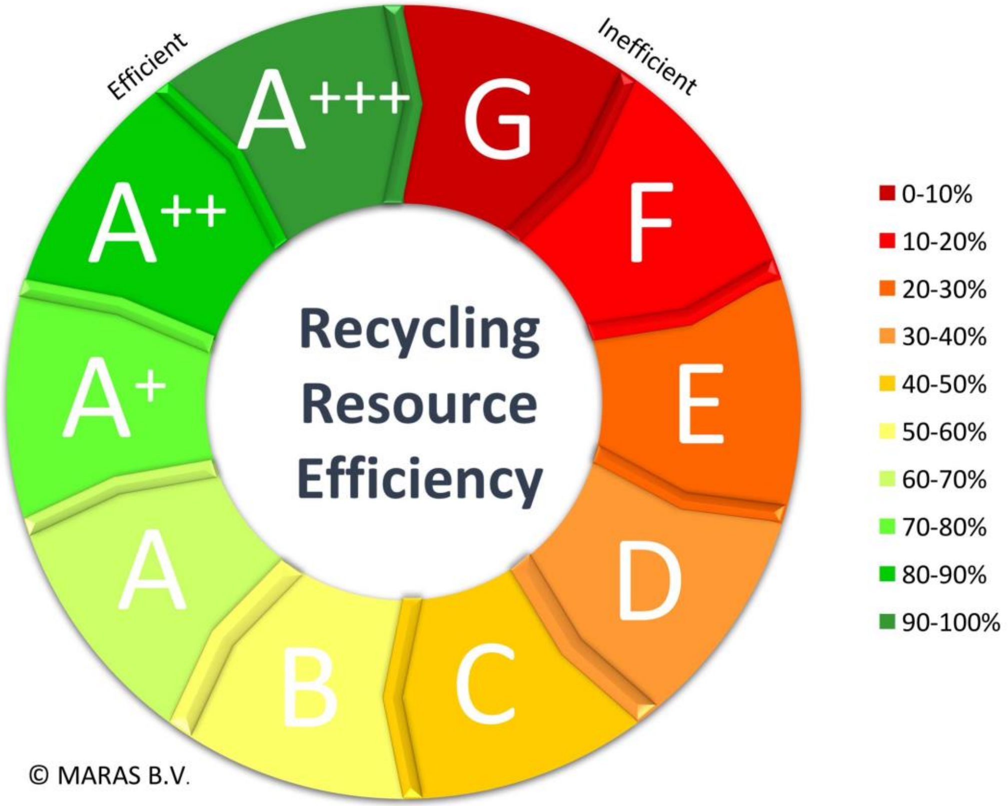
If product design can keep thermodynamically compatible materials close togheter, then metallurgical technology can deal with them.



23/05/2024

Reuter, Markus A., and Ilkka V. Kojo. "Challenges of metal recycling." *Materia* 2.2012 (2012): 50-57.

Design for Recycling- Ecodesign Strategy



Reuter, Markus A., and Ilkka V. Kojo. "Challenges of metal recycling." *Materia* 2.2012 (2012): 50-57.

The R Strategies

The 9R framework or R-ladder listing circularity strategies within the production chain, in order of priority

Circular economy

	Strategies	Description
Smarter product use and manufacture	R0 refuse	Make product redundant by abandoning its function or by offering the same function with a radically different product
	R1 rethink	Make product use more intensive, e.g., through sharing or multi-functionality
	R2 reduce	Increase efficiency in product manufacture or use so less natural resources are consumed
Extend lifespan of product and its parts	R3 reuse	Reuse of the discarded product by another consumer, when it is still in good condition and fulfils its original function
	R4 repair	Repair and maintenance of defective product so it can be used with its original function
	R5 refurbish	Restore an old product and bring it up to date, so it meets today's standards
	R6 remanufacture	Use parts of discarded product in a new product with the same function
	R7 repurpose	Use discarded product or its parts in a new product with a different function
Useful application of materials	R8 recycle	Process materials to obtain the same (high grade) or lower (low grade) quality
	R9 recover	Incineration of materials with energy recovery

Linear economy

Meskers, Christina, Ernst Worrell, and Markus A. Reuter, eds. *Handbook of Recycling: State-of-the-art for Practitioners, Analysts, and Scientists*. Elsevier, 2023.

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Thank you