UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

Potential Alternative Utilization of Manganese Nodules

Ng. Hong VU

Utilization of leaching residues as sorbents

Reductive leaching:

- 90 °C, l/s= 10:1, ~ 20g SO_2/l, ~ 100g H_2SO_4/l, 60 min

Sorbents preparation:

- A1: original leaching residue
- A2/Cl: A1 activated in 10% vol. HCl
- A2/N: A1 activated in 10% vol. HNO_3
- A3/1: A1 thermally activated at 250 °C, 8 h
- A3/Cl: A2/Cl thermally activated at 250 °C, 8 h
- A4/Cl: A2/Cl mechanically activated in a mill at 600 rpm, 30 min
- A5/Fe^{II}: precipitation of Fe^{II} on A1, 24 h, $FeSO_4$ under N_2
- A5/Fe^{III}: precipitation of Fe^{III} on A1, 24 h, $Fe(NO_3)_3$, NaOH
- A5/Al^{III}: precipitation of Fe^{III} on A1, 24 h, $AlCl_3$, NaOH

Sorption tests:

- 0.1g of a sorbent, 50 mL, 100 mg/L of a selected meta

Utilization of leaching residues as sorbents

Results:

Chemical composition of sorbents [%]

	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Sr	Ba	Pb
A1	0.89	0.41	5.95	38.71	1.10	0.03	2.39	1.42	0.67	1.66	0.29	3.60	0.24
A2/N	1.06	0.42	6.73	41.87	0.92	0.03	2.48	1.34	0.63	1.74	0.15	3.62	0.14
A2/Cl	0.87	0.53	6.28	40.24	0.62	0.03	2.36	1.29	0.52	1.51	0.14	4.12	0.16
A3/1	0.91	0.42	6.01	40.30	1.14	0.04	2.50	1.35	0.69	1.72	0.30	4.01	0.29
A3/Cl	0.88	0.53	6.19	40.18	0.62	0.03	2.41	1.28	0.53	1.52	0.14	4.14	0.15
A4/Cl	0.88	0.50	6.15	41.04	0.54	0.03	2.34	1.28	0.52	1.50	0.15	3.50	0.15
A5/Fe^{II}	1.00	0.45	6.33	39.16	1.43	0.03	2.37	1.40	0.64	3.07	0.27	3.95	0.25
A5/Fe^{III}	1.01	0.45	6.17	39.73	0.89	0.02	2.48	1.39	0.66	4.89	0.18	3.23	0.14
A5/Al^{III}	0.67	0.23	13.77	27.78	0.68	0.79	3.21	1.14	0.46	1.18	0.09	2.06	0.15

Utilization of leaching residues as sorbents

Results:

Mineralogical composition of the sorbent A1

Ref. Code	Mineral Name	Chemical Formula	SemiQuant [%]
00-046-1045	Quartz, syn	SiO_2	19
00-005-0448	Barite	$BaSO_4$	5
04-007-5092	Albite	$NaAlSi_3O_8$	32
01-086-0438	Orthoclase	$K(AlSi_3O_8)$	11
01-073-9865	Muscovite-2M1, ferrian	$K_{0.92}Na_{0.08}Al_{1.78}Fe_{0.22}Mg_{0.1}(Al_{0.83}Si_{3.17}O_{10})(OH)_{1.56}O_{0.25}F_{0.19}$	28
04-011-5452	Dickite-2M1	$Al_2Si_2O_5(OH)_4$	5

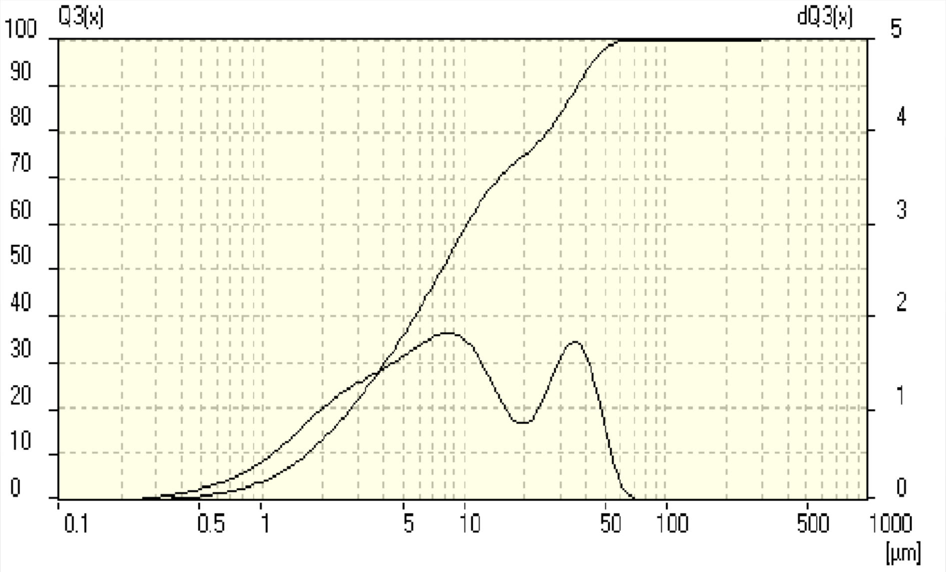
Utilization of leaching residues as sorbents

Results:

Specific surface of sorbents, measured by BET [m2/g] and their moisture

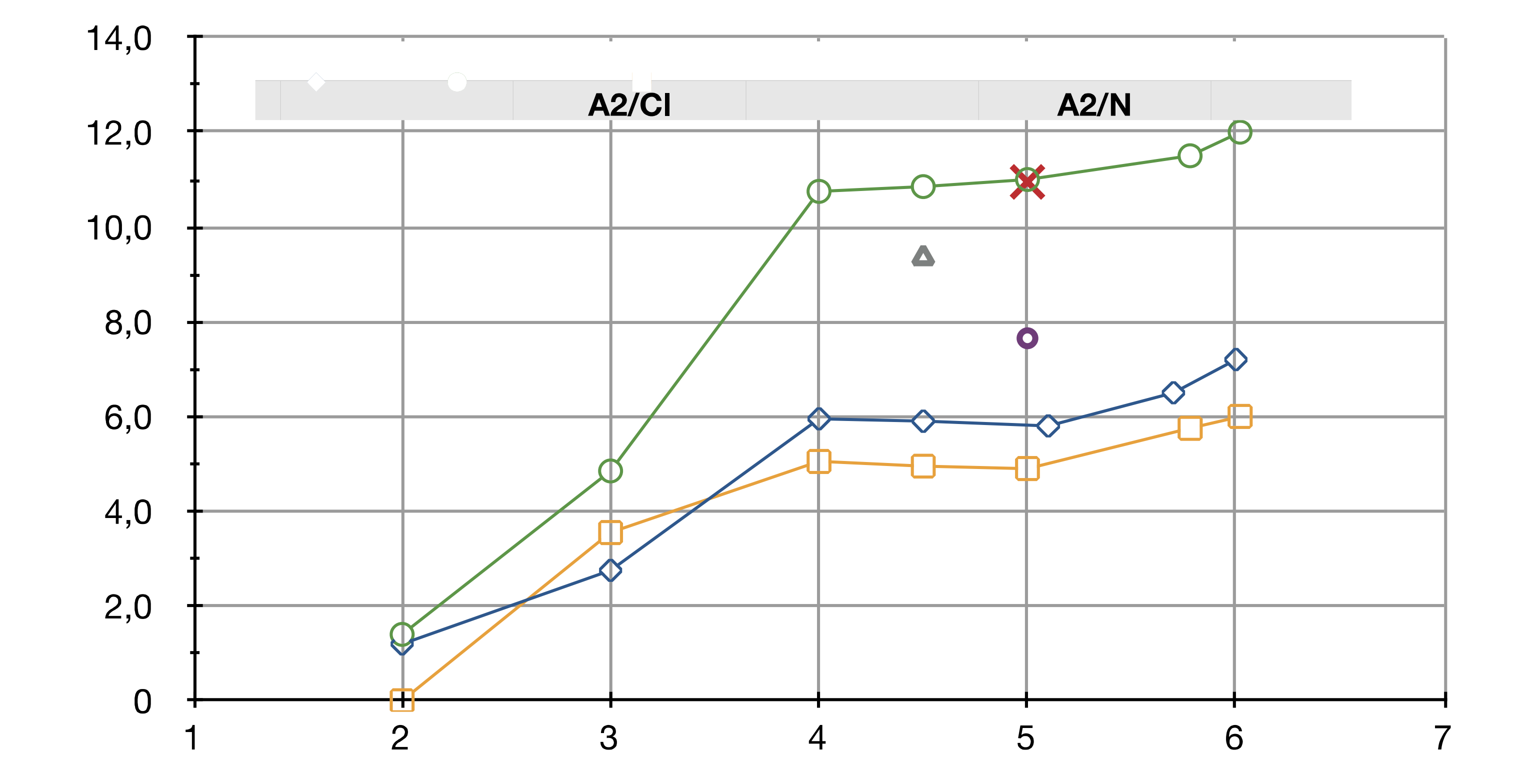
	A1	A2/N	A2/Cl	A3/1	A3/Cl	A4/Cl	A5/Fe^{II}	A5/Fe^{III}	A5/Al^{III}
Specific surface	234	227	229	220	211	216	274	253	298
Moisture	6.07	5.13	5.52	2,15	2.30	8.78	2.42	2.80	3.22

Particle size distribution of the sorbent A1



Utilization of leaching residues as sorbents

Results:



Effect of pH on the adsorption of Pb onto adsorbents: 200rpm, 8h

Utilization of leaching residues as sorbents

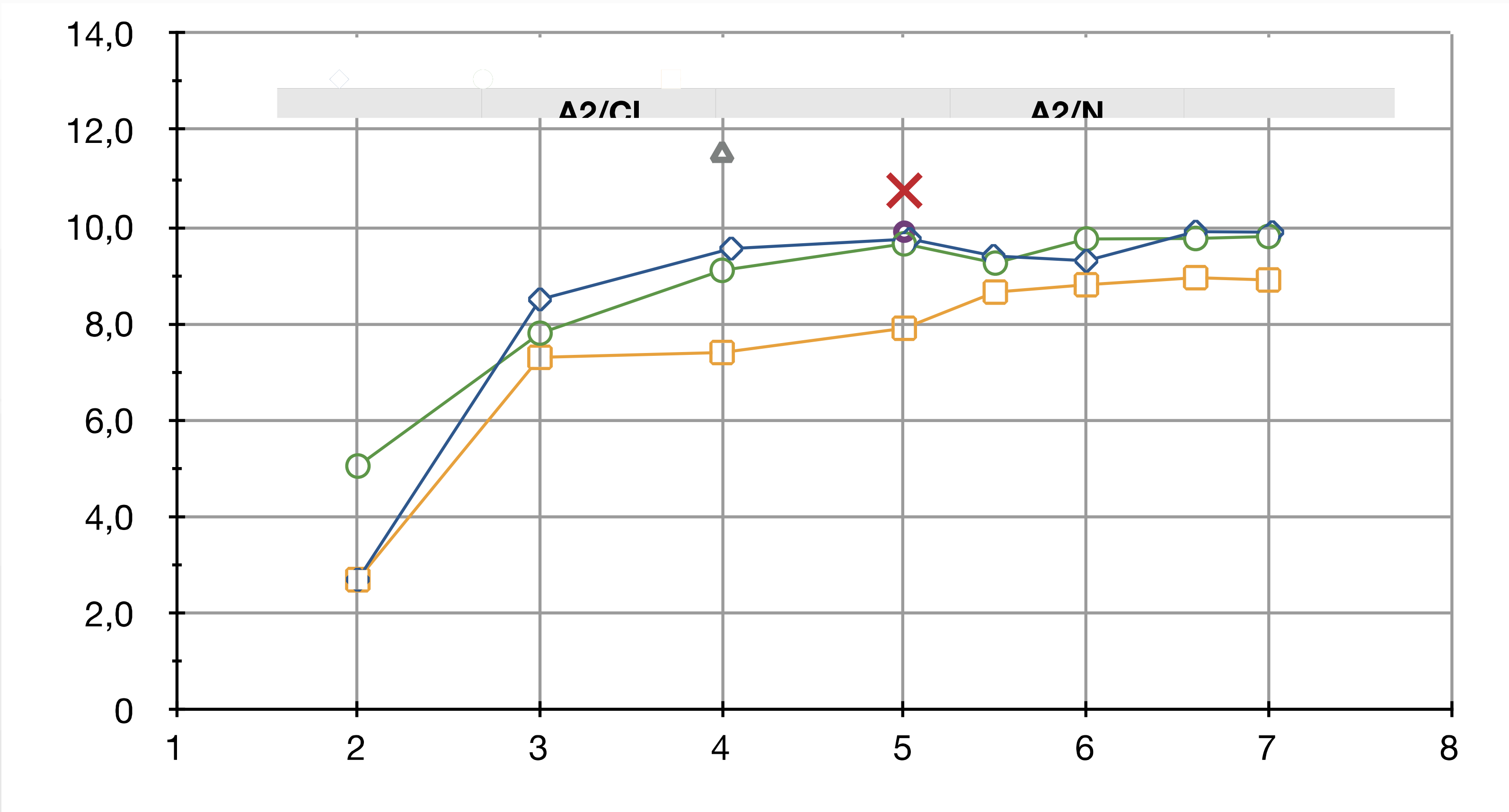
Results:

N

Dependence of the Pb uptake on adsorption time: 200rpm, pH 5.05

Utilization of leaching residues as sorbents

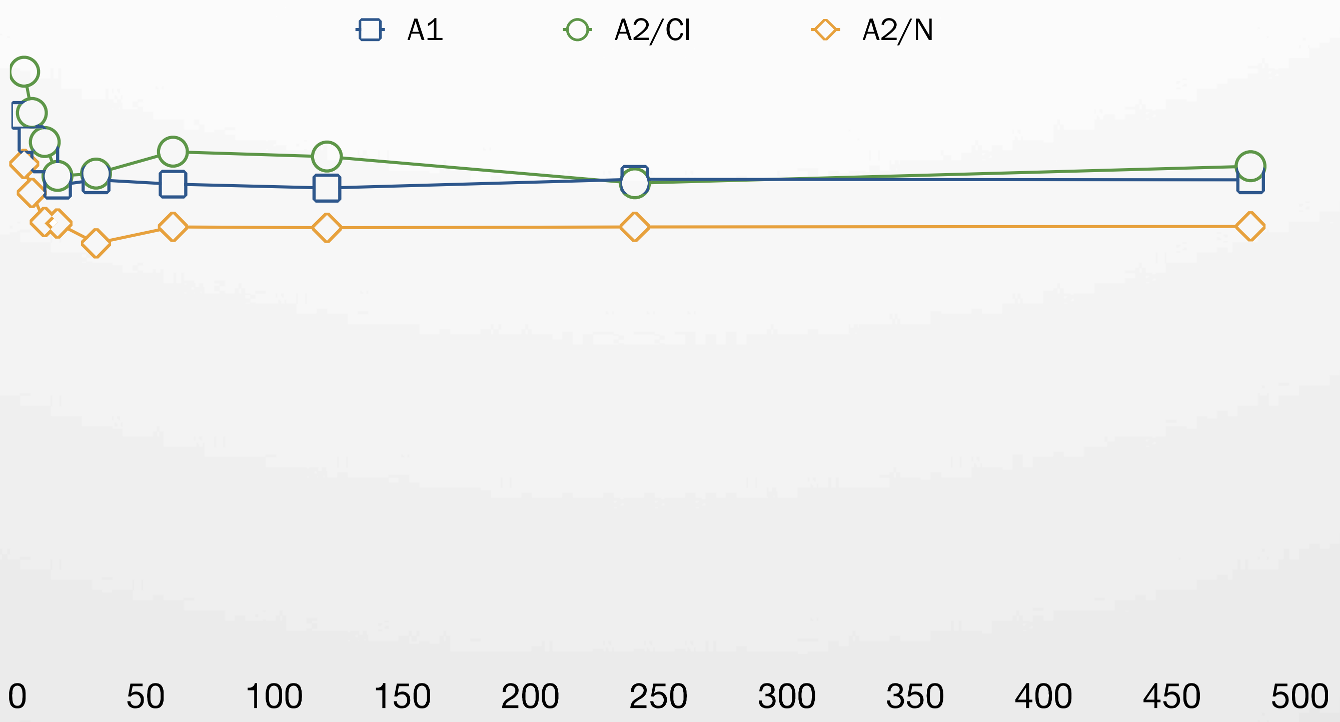
Results:



Effect of pH on the adsorption of Cd onto adsorbents: 200rpm, 8h

Utilization of leaching residues as sorbents

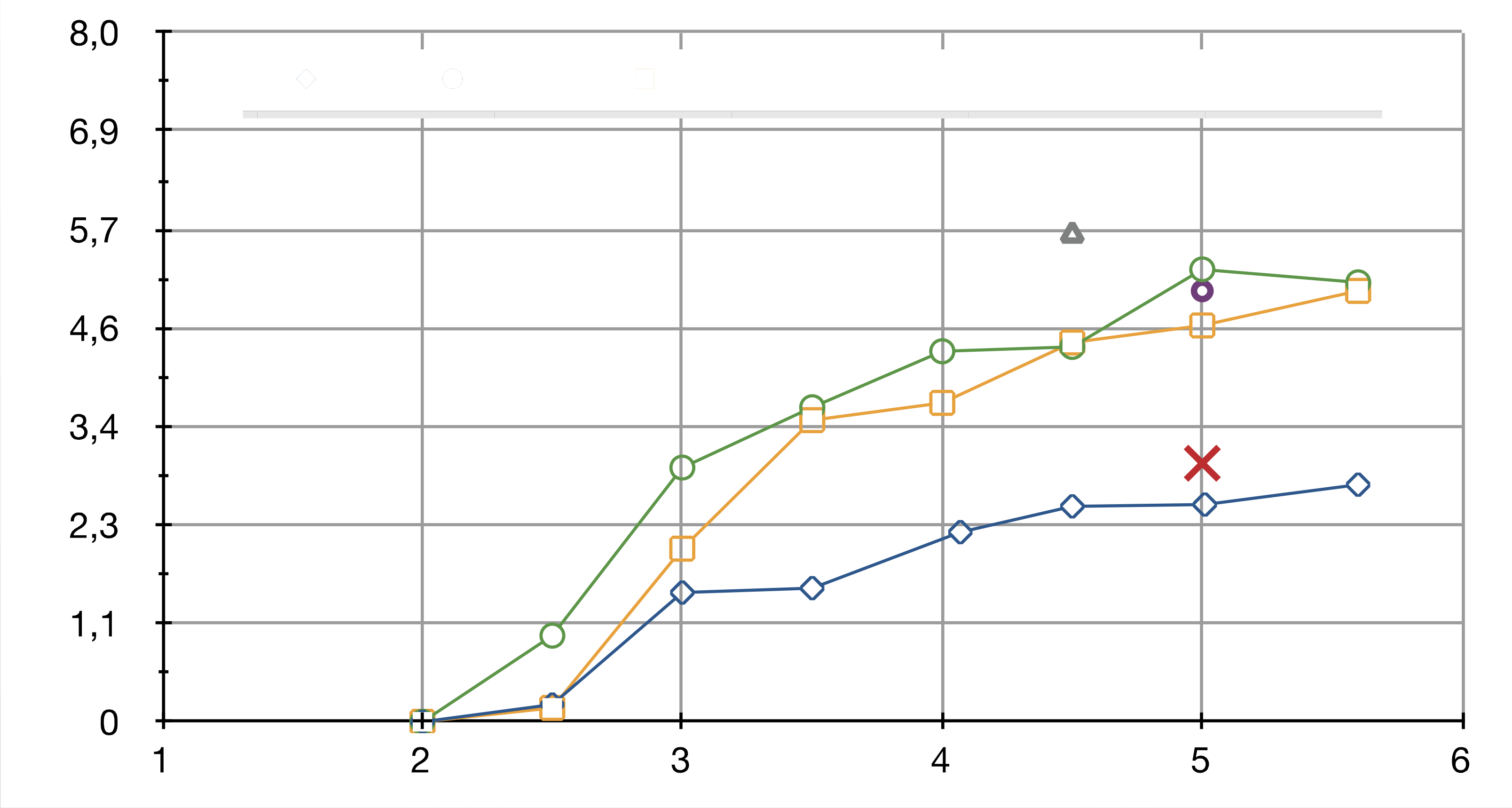
Results:



Dependence of the Cd uptake on adsorption time: 200rpm, pH 6.0

Utilization of leaching residues as sorbents

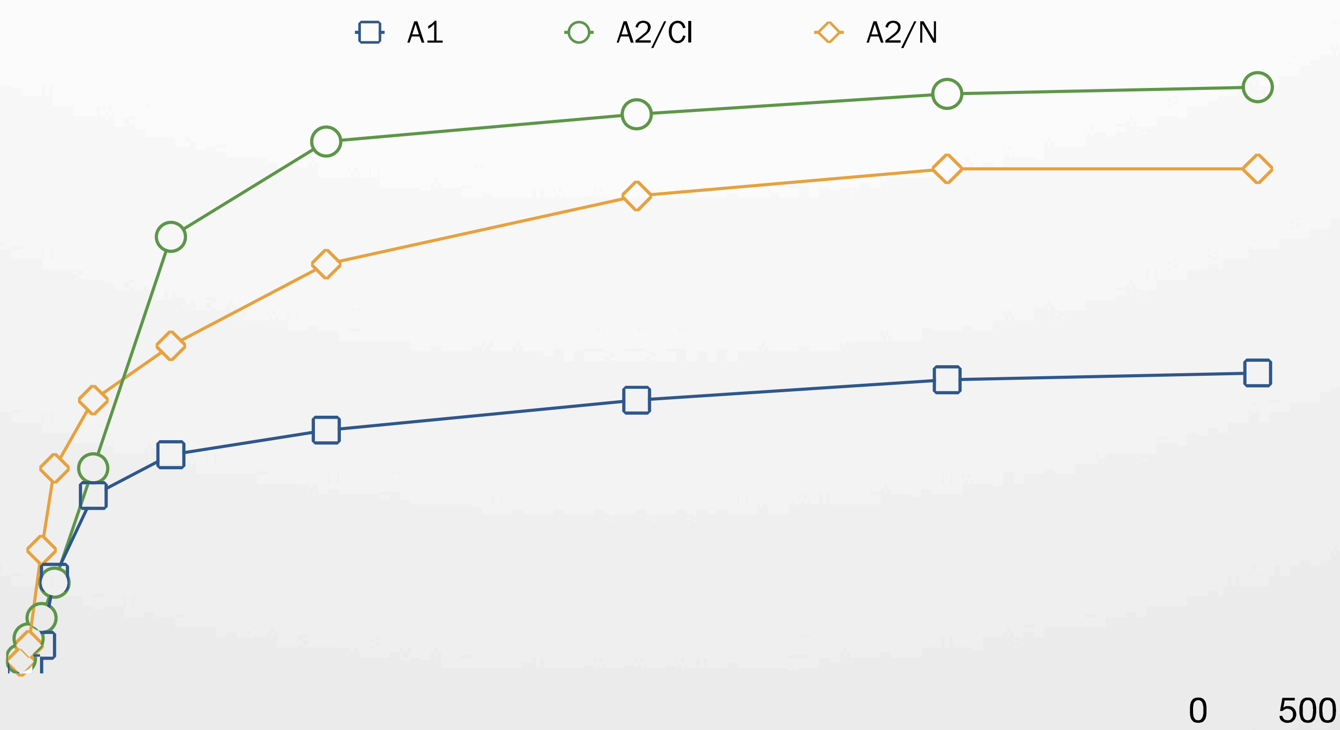
Results:



Effect of pH on the adsorption of Cu onto adsorbents: 200rpm, 8h

Utilization of leaching residues as sorbents

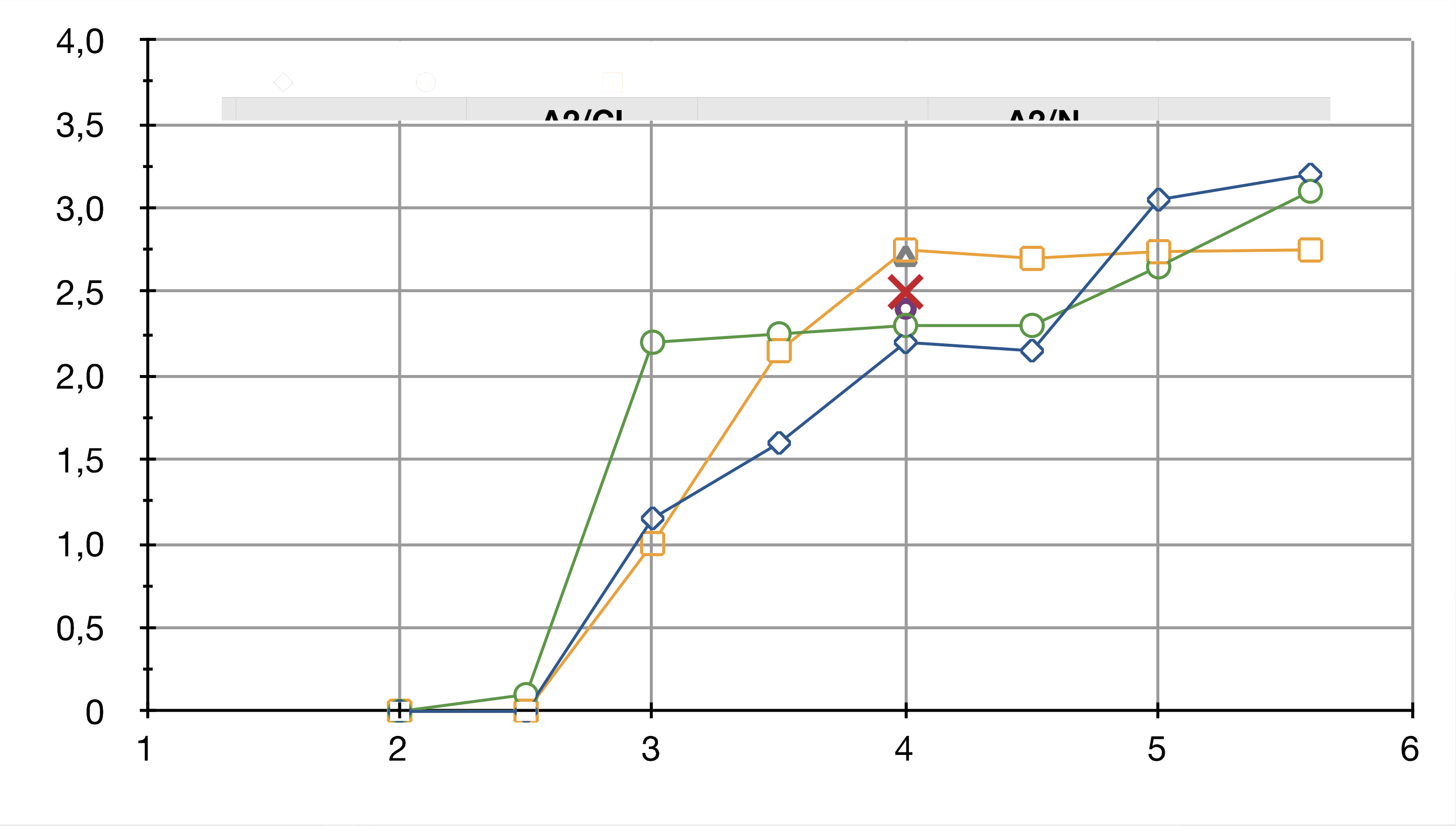
Results:



Dependence of the Cu uptake on adsorption time: 200rpm, pH 4

Utilization of leaching residues as sorbents

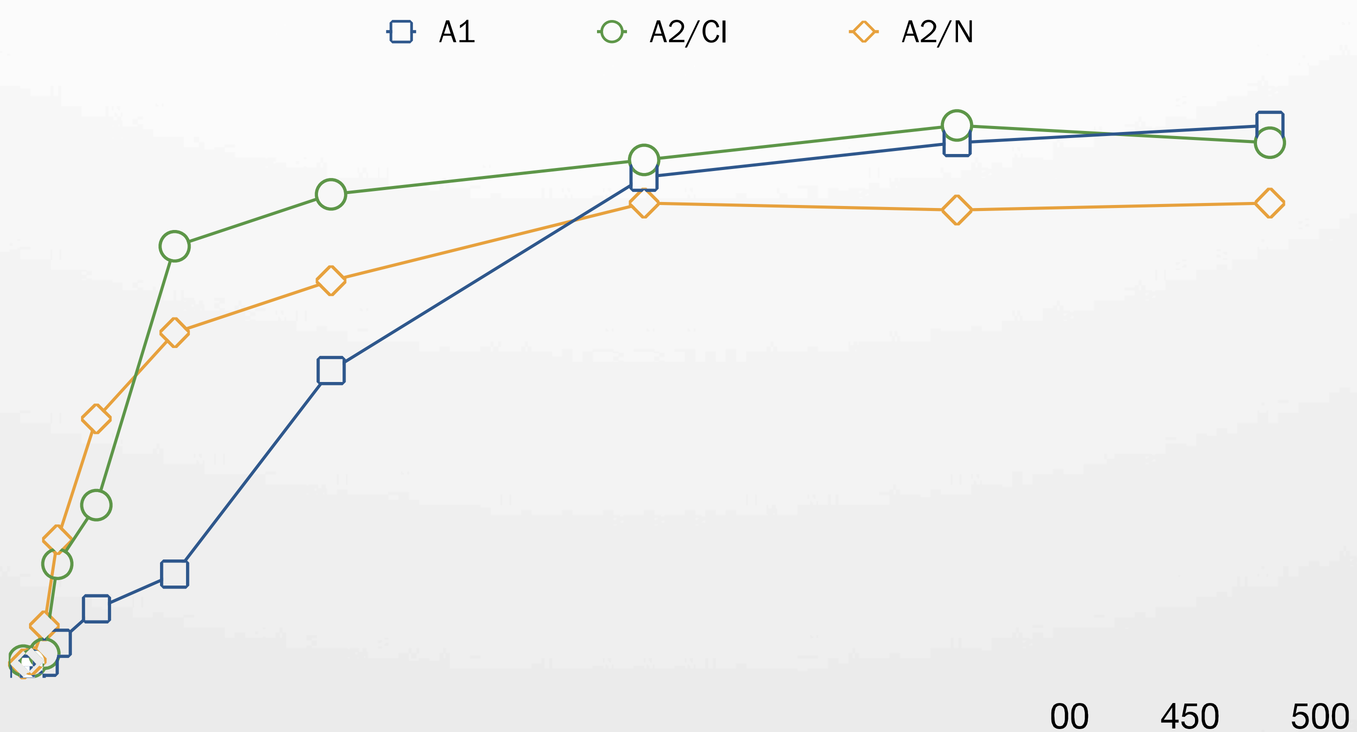
Results:



Effect of pH on the adsorption of Ni onto adsorbents: 200rpm, 8h

Utilization of leaching residues as sorbents

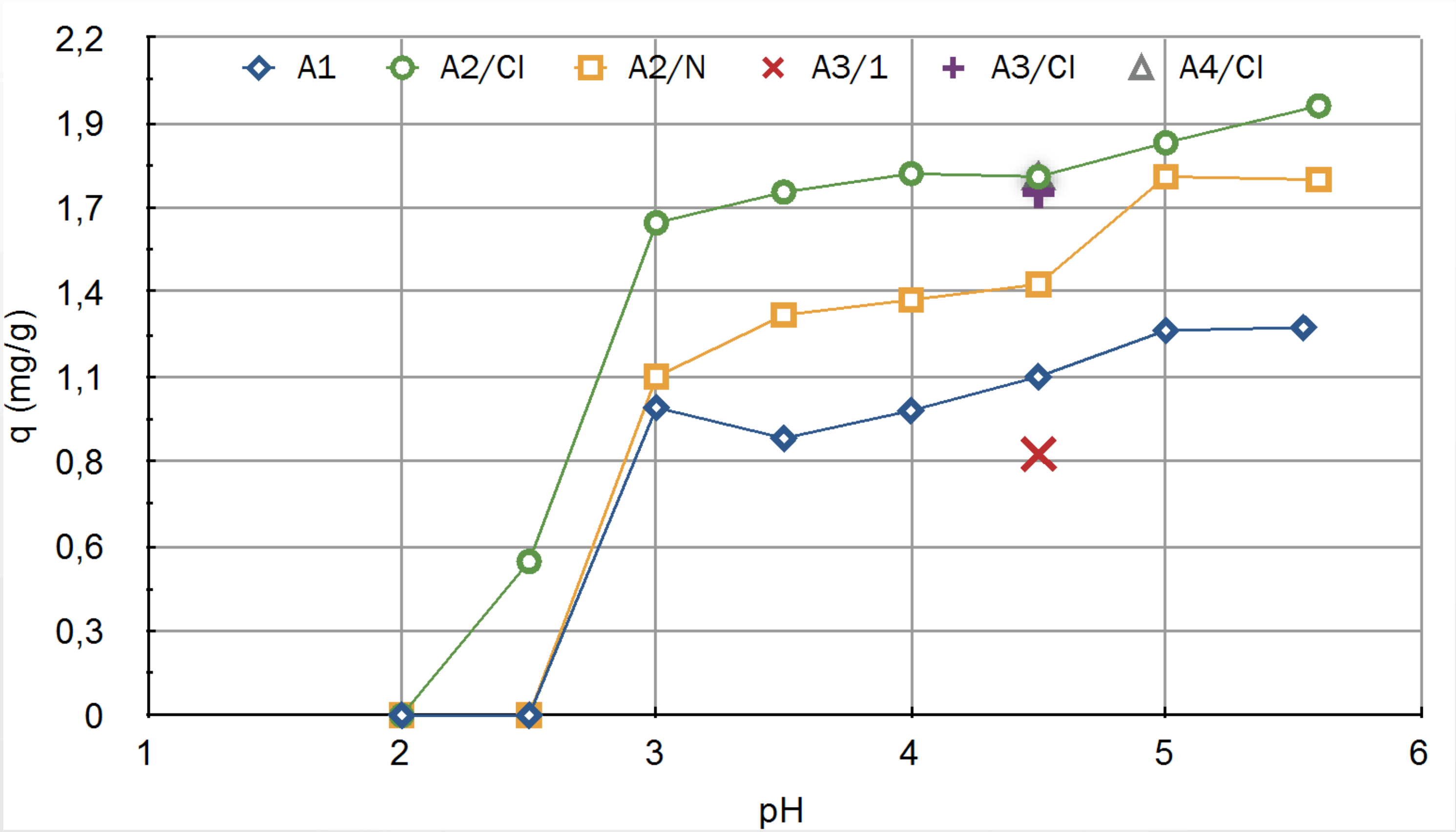
Results:



Dependence of the Ni uptake on adsorption time: 200rpm, pH 5.5

Utilization of leaching residues as sorbents

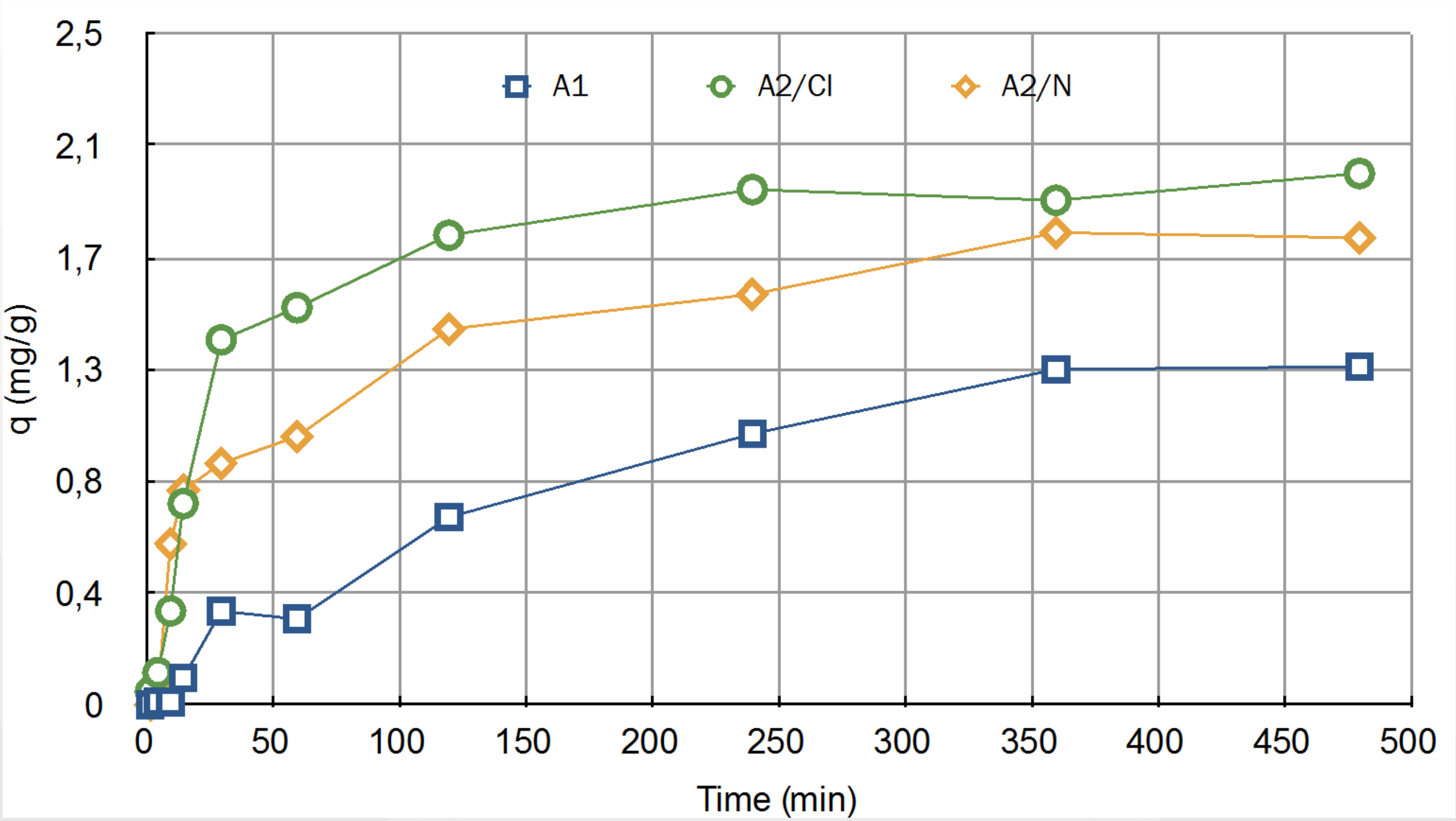
Results:



Effect of pH on the adsorption of Co onto adsorbents: 200rpm, 8h

Utilization of leaching residues as sorbents

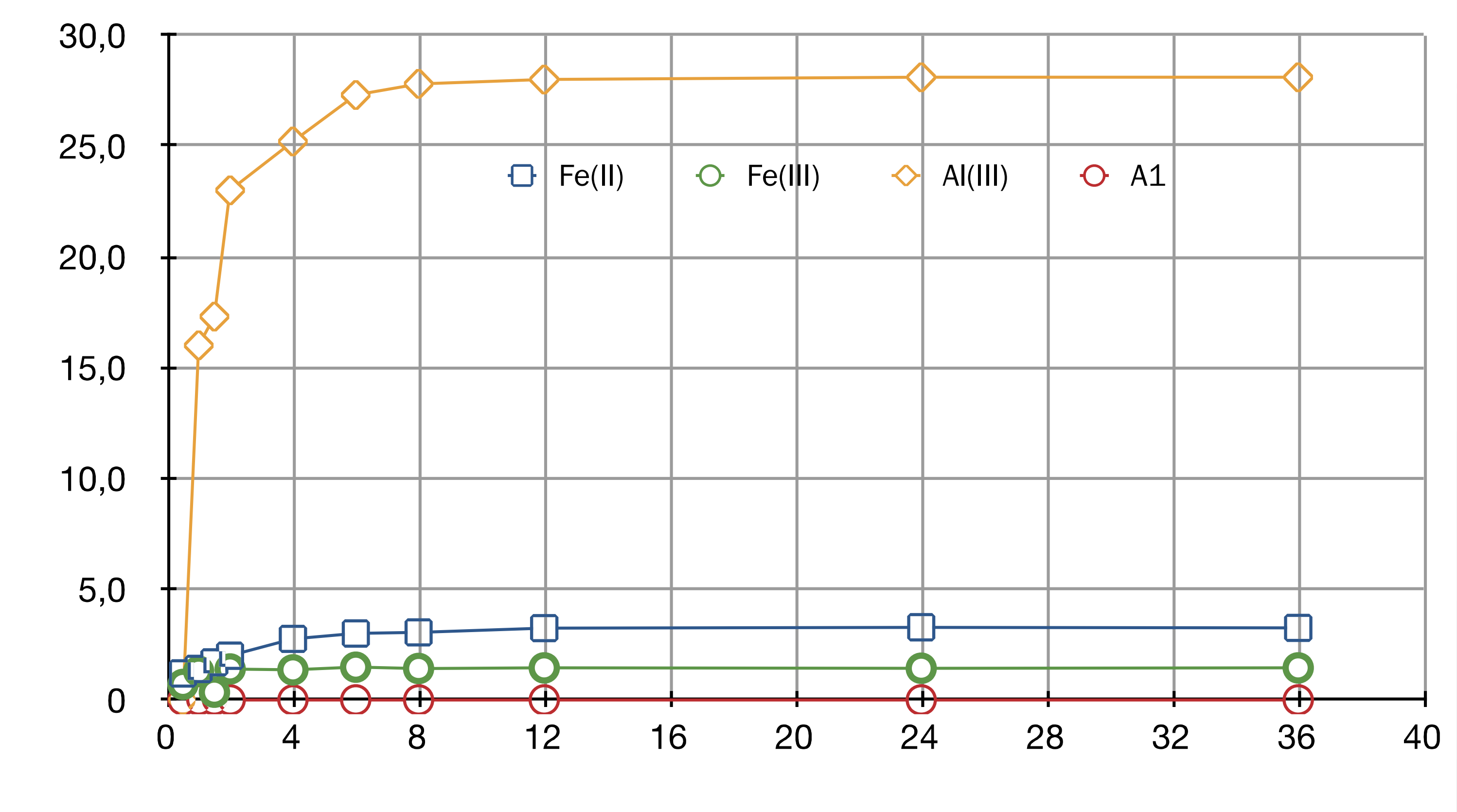
Results:



Dependence of the Co uptake on adsorption time: 200rpm, pH 5

Utilization of leaching residues as sorbents

Results:



Dependence of the As uptake on adsorption time: 250rpm, pH 7.0

Utilization of leaching residues as sorbents

Results:

Comparison of maximum As(V) adsorption capacities of different adsorbents

Adsorbent	Initial pH	Concentration range (mg L^{-1})	Adsorption capacity (mg g^{-1})	Reference
Nanohydrous Fe-Ti mixed oxide	7	5 - 150	14.3	(Gupta and Ghosh 2009)
TiO_2 nanoparticle	7.6	5 - 90	20.53	(Nabi 2009)
Crystalline hydrous Fe_2O_3	3-4	50 - 250	25	(Manna et al. 2003)
Nanostructure Fe(III)-Zr(IV) bimetal mixed oxide (NHIZO)	7	5 - 150	9.36	(Gupta et al. 2009)
CuO nanoparticles	8	0.1 - 100	22.6	(Martinson and Reddy 2009)
Nanostructured akaganeite	7.5	5 - 20	1.80	(Deliyanni et al. 2003)
Fe–Zr binary oxide	7.0	5 - 40	46.1	(Ren et al. 2011)
Al_2O_3 /$Fe(OH)_3$	7.2	7.5 - 135	36.7	(Hlavay and Polyák 2005)
CuO nanoparticles	8.0	0.1- 100	22.6	(Martinson 2009)
A5/Fe^{II}	7.0	100	3.25	
A5/Fe^{III}	7.0	100	1.45	**Present work**
A5/Al	7.0	100	**28.1**	

Utilization of leaching residues as sorbents

Conclusions:

- Prepared adsorbents are effective in a fast removal of Pb and Cd.
- Chemical and mechanochemical (milling) activation generally increased the maximum adsorption capacity.
- The activated sorbents can be used to remove Cu, Ni and Co from aqueous solution.
- Nanostructured sorbents were proved to be effective for arsenic removal. Especially the adsorbent A5/A^{IIII} based on nanoparticles of $Al(OH)_3$can be considered one of the best materials for an effective arsenic removal at low cost

↓

Using leaching residues to treat waste water
in hydrometallurgical plants

Nodules and Metals for E-mobility - LITHIUM

Elements in nodules for emerging and next generation technologies[3]

Element	CCZ nodules	Indian Ocean nodules
	Mean [ppm]	Mean [ppm]
Li	131	110
Mo	590	600
Sc	11	25
Th	15	76
Y	96	108
La	114	129
Ce	284	486
Pr	33.4	33
Nd	140	146
Sm	34	32.4
Eu	8.03	7.83
Gd	31.8	32
Tb	4.98	5.0
Dy	28.5	26.5
Ho	5.35	4.92
Er	14.6	12.9
Tm	2.11	2.00
Yb	13.7	11.8
Lu	2.05	1.93

[3] R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

3 millions tones of nodules

↓

400 tones of lithium metal

↓

2,500 tones of Li_2CO_3

↓

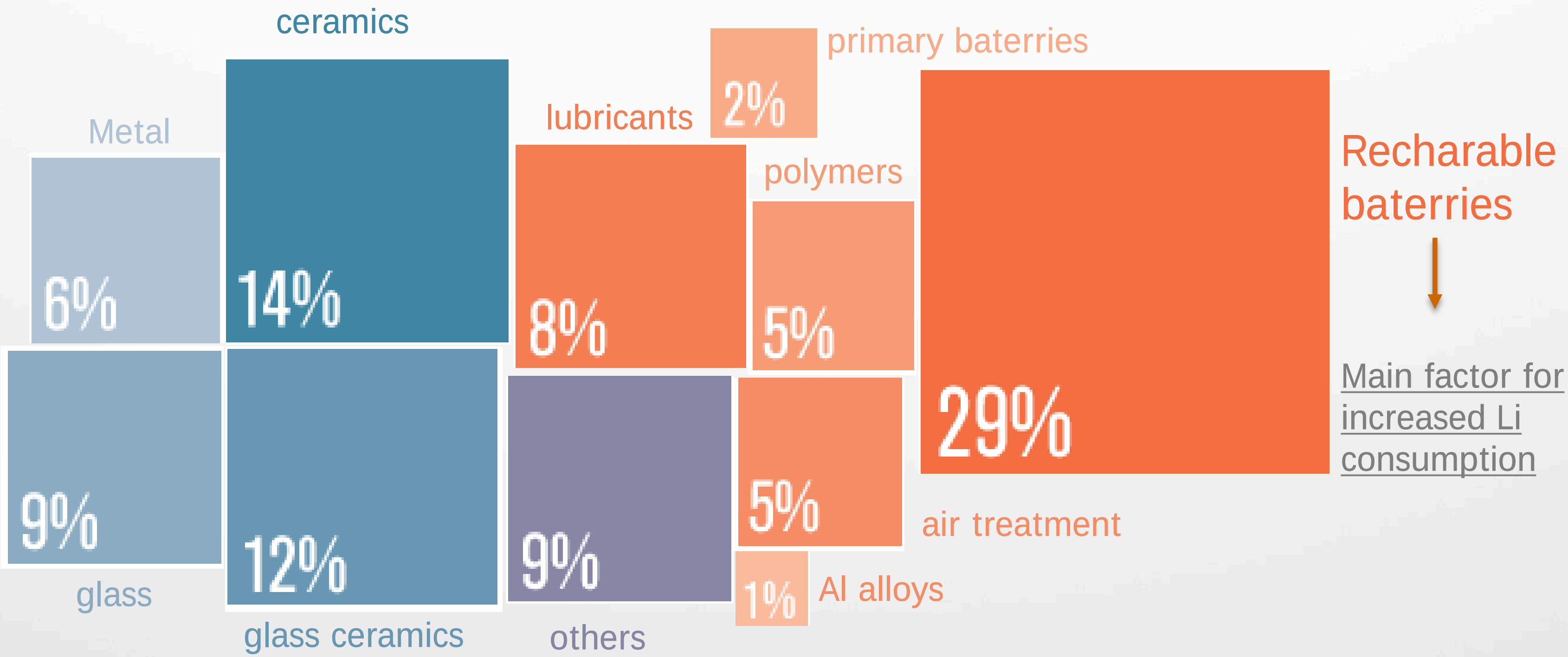
1% of the Li world production

↓

37,5 millions USD

LITHIUM – a key raw material for modern technologies

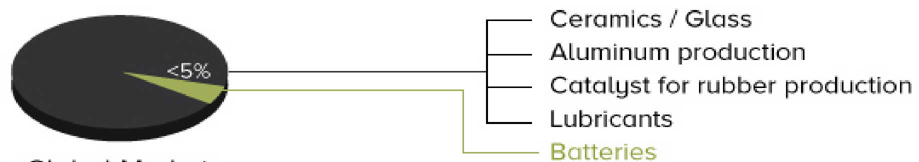
Li consumption is usually divided to
Chemical and **Technical**



LITHIUM – a key raw material for modern technologies

2001

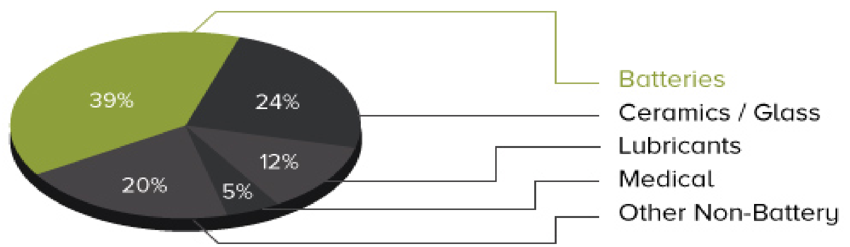
Many years ago, lithium was used in a variety of industrial purposes.



Global Market
70,000 tonnes LCE
Source: USGS

2015

Today, the major use by far is batteries.

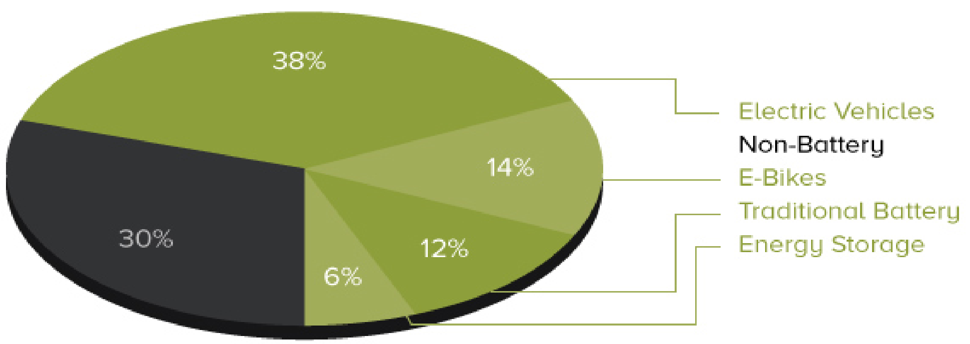


Global Market
163,000 tonnes LCE
Source: Global Lithium LLC

And in the future?

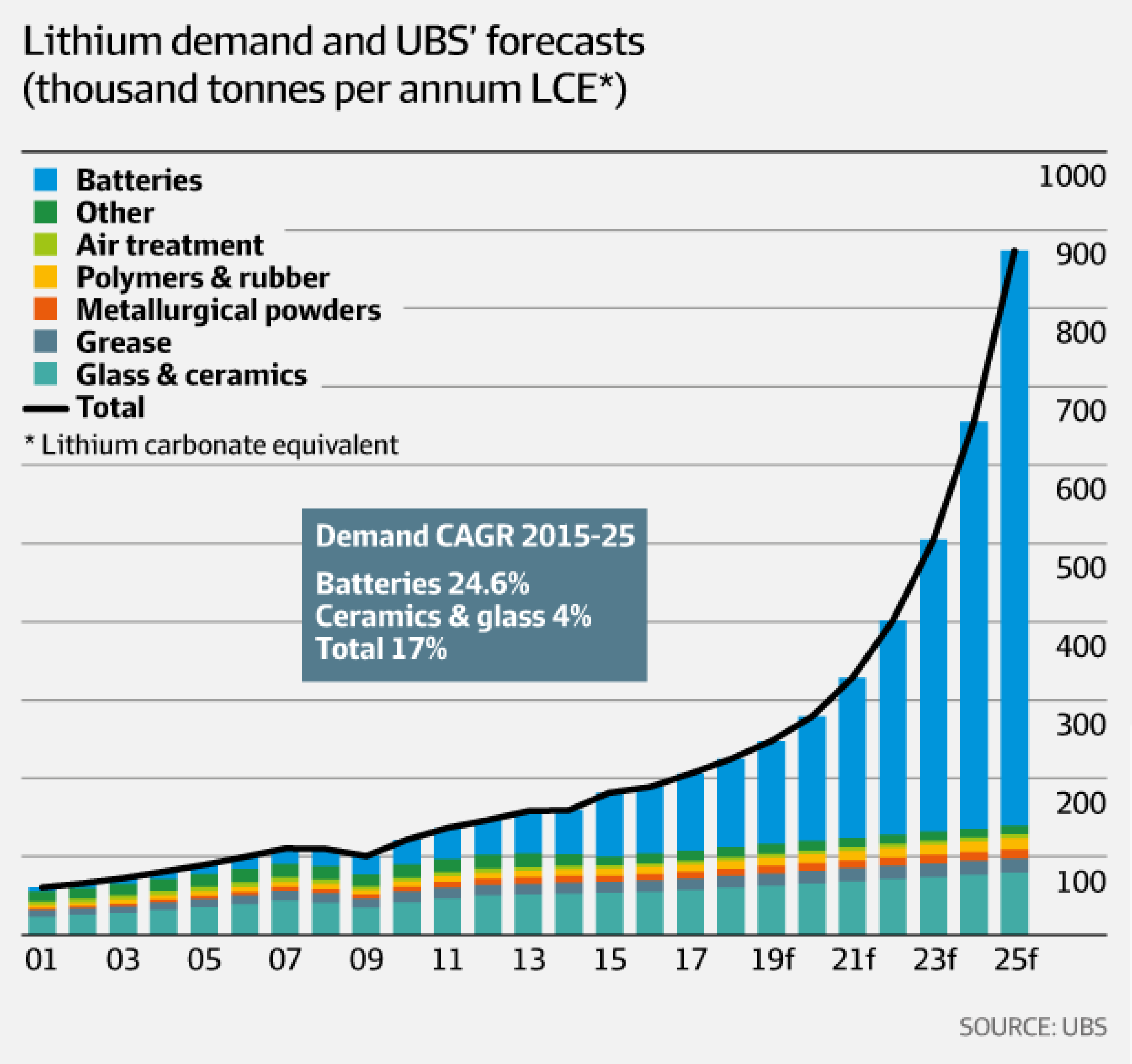
2025

The battery market alone will be almost 2x bigger than the entire lithium market today.



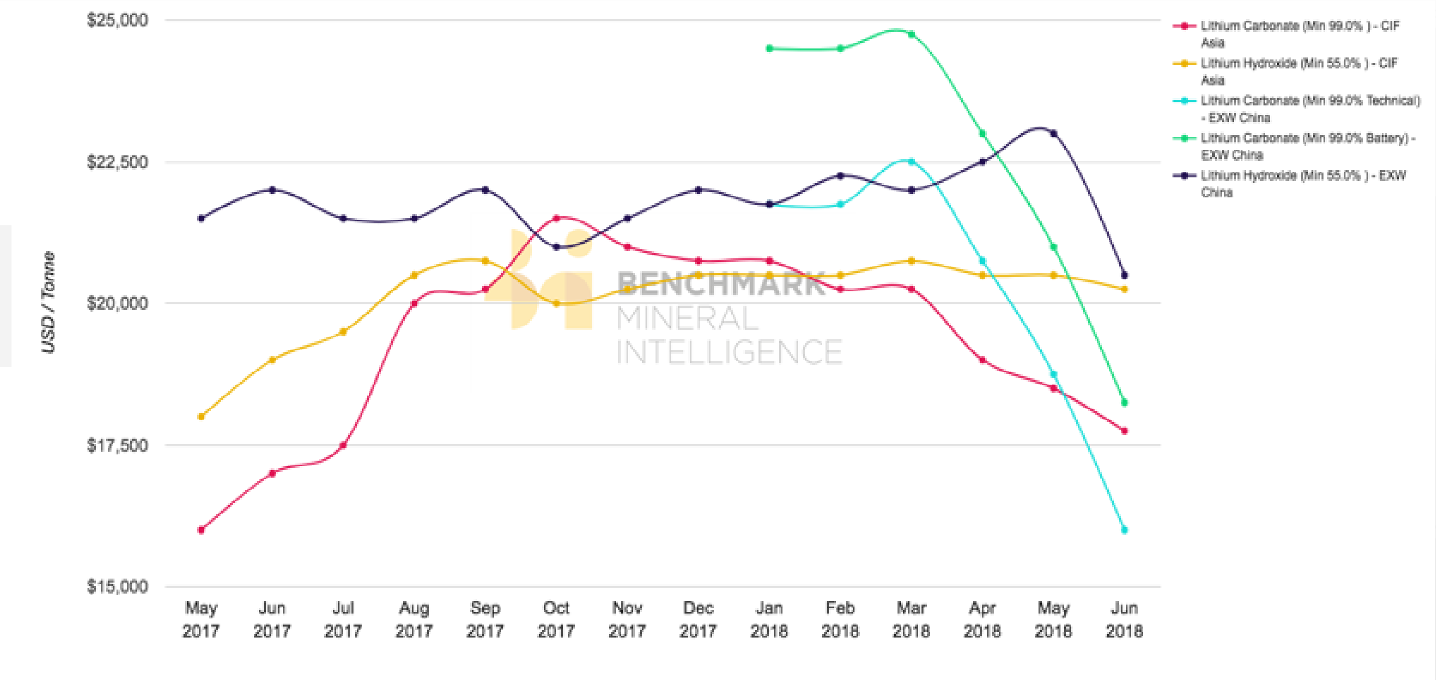
Global Market
534,000 tonnes LCE
Source: Deutsche Bank

LITHIUM – a key raw material for modern technologies

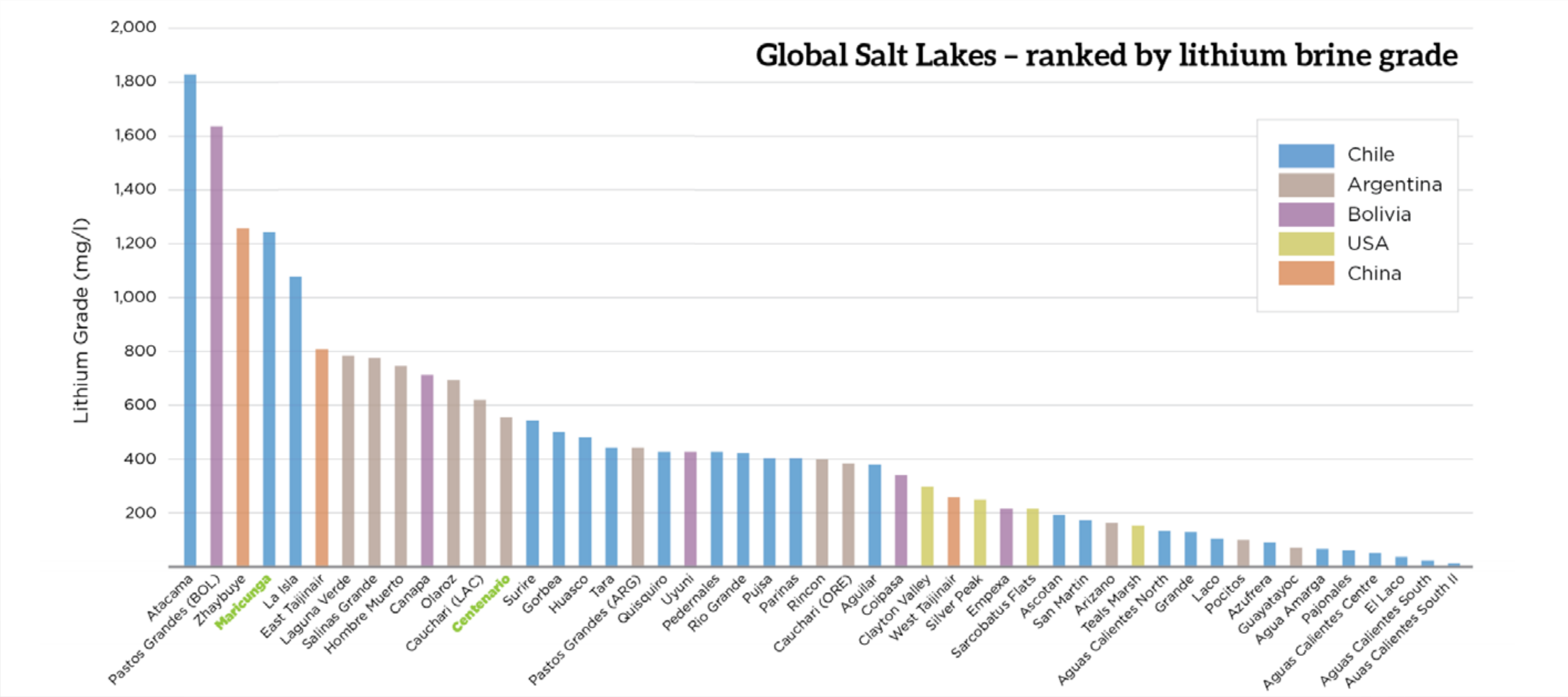


LITHIUM – a key raw material for modern technologies

Price developlment of main marketable lithium compounds

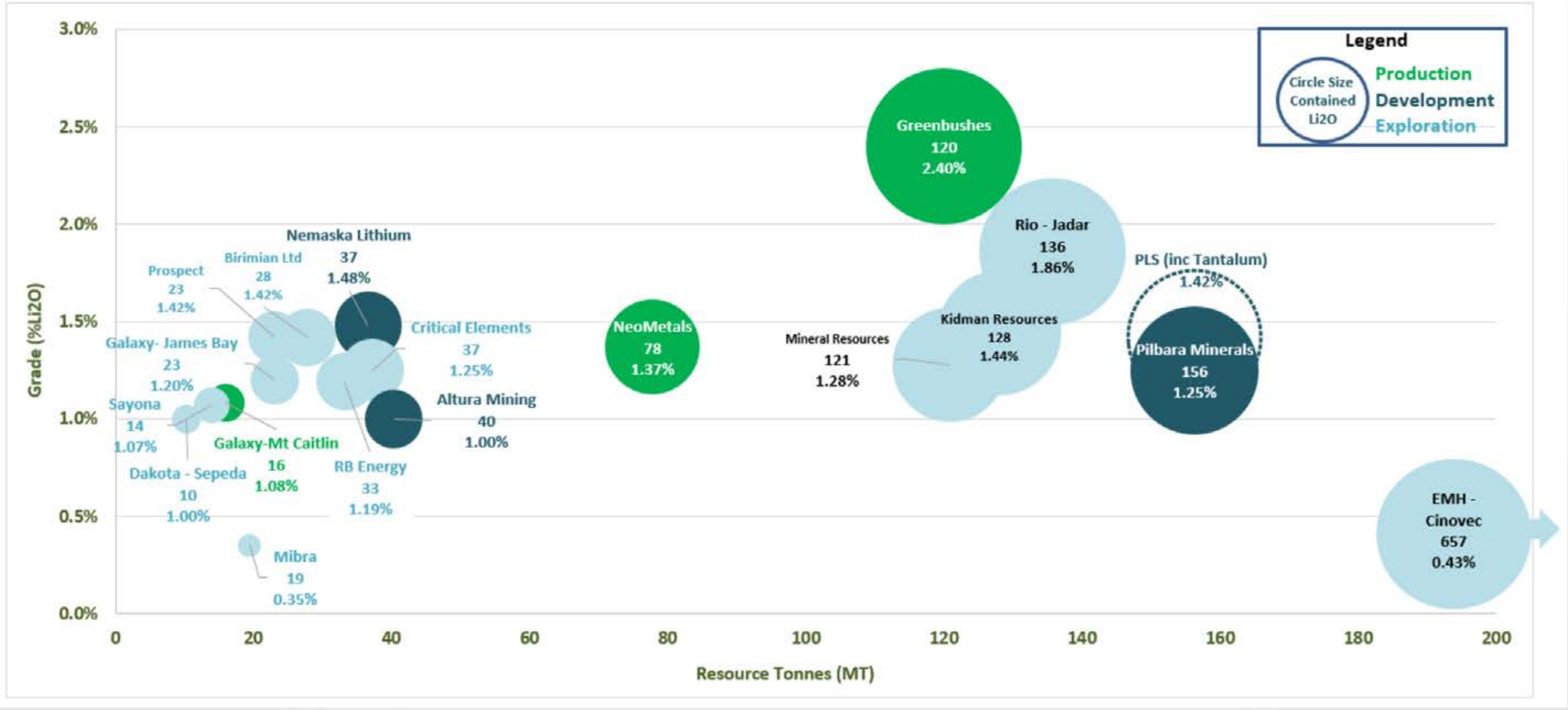


LITHIUM – a key raw material for modern technologies



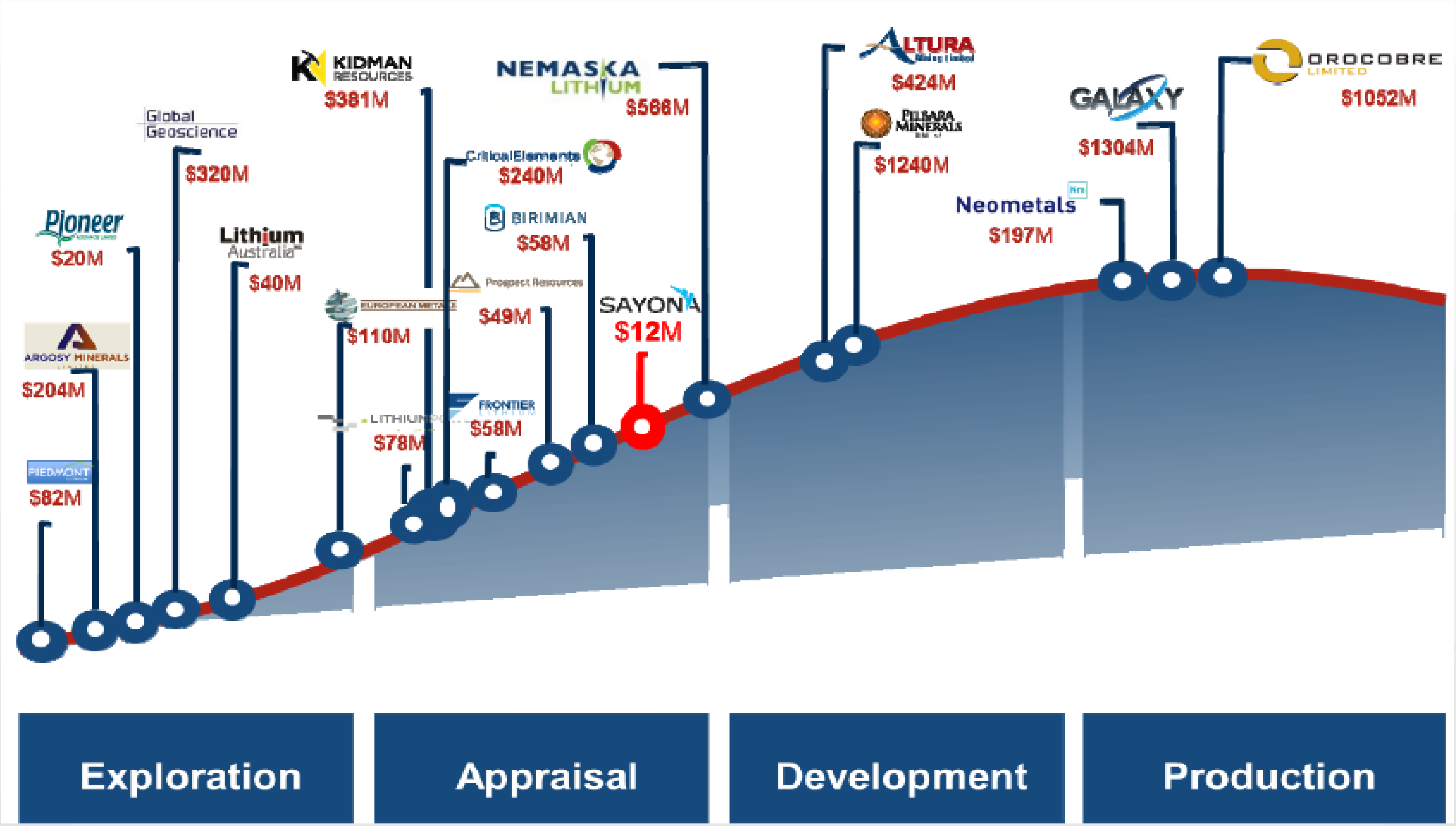
LITHIUM – a key raw material for modern technologies

Lithium minerals



LITHIUM – a many junior miners want to join the league of big

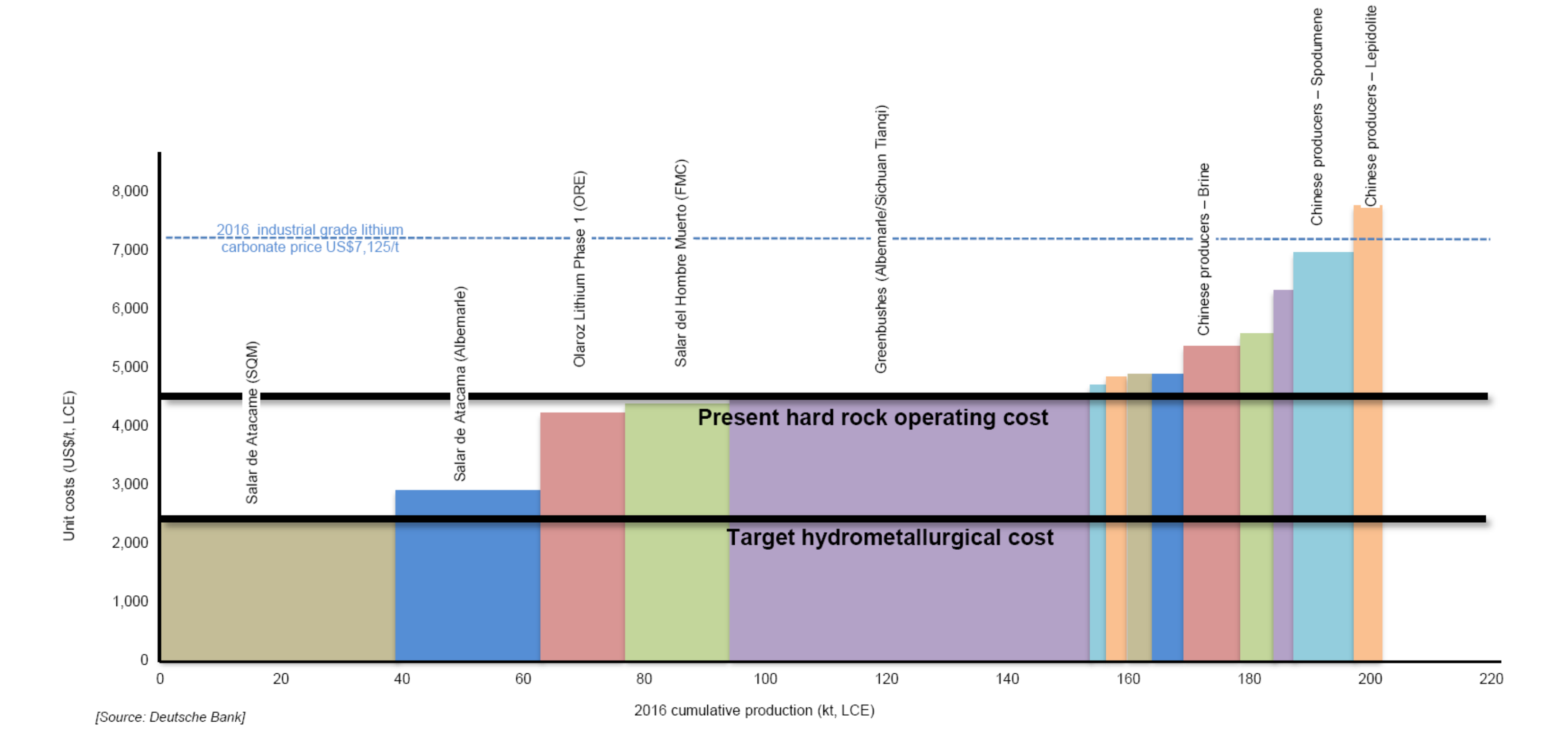
4



LITHIUM – OPEX price comparision

1 t of zinnwaldite concentrate – 100 USD

1 t of spodumene concentrate – 550 USD



Nodules and Metals for E-mobility - LITHIUM

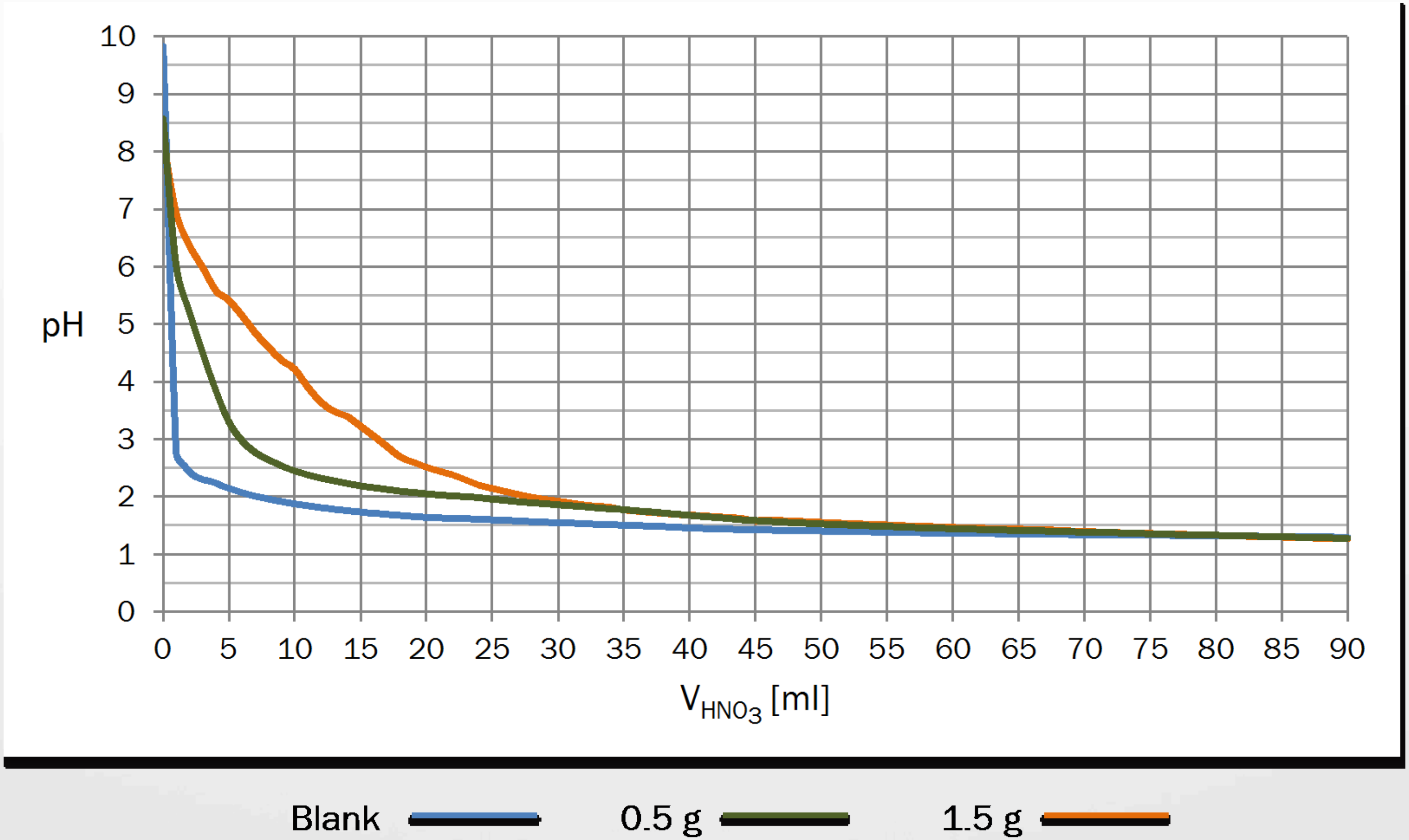
New approaches needed for recovering Li at low concentration

↓

Direct usage of manganese nodules to recover Li

[3] R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

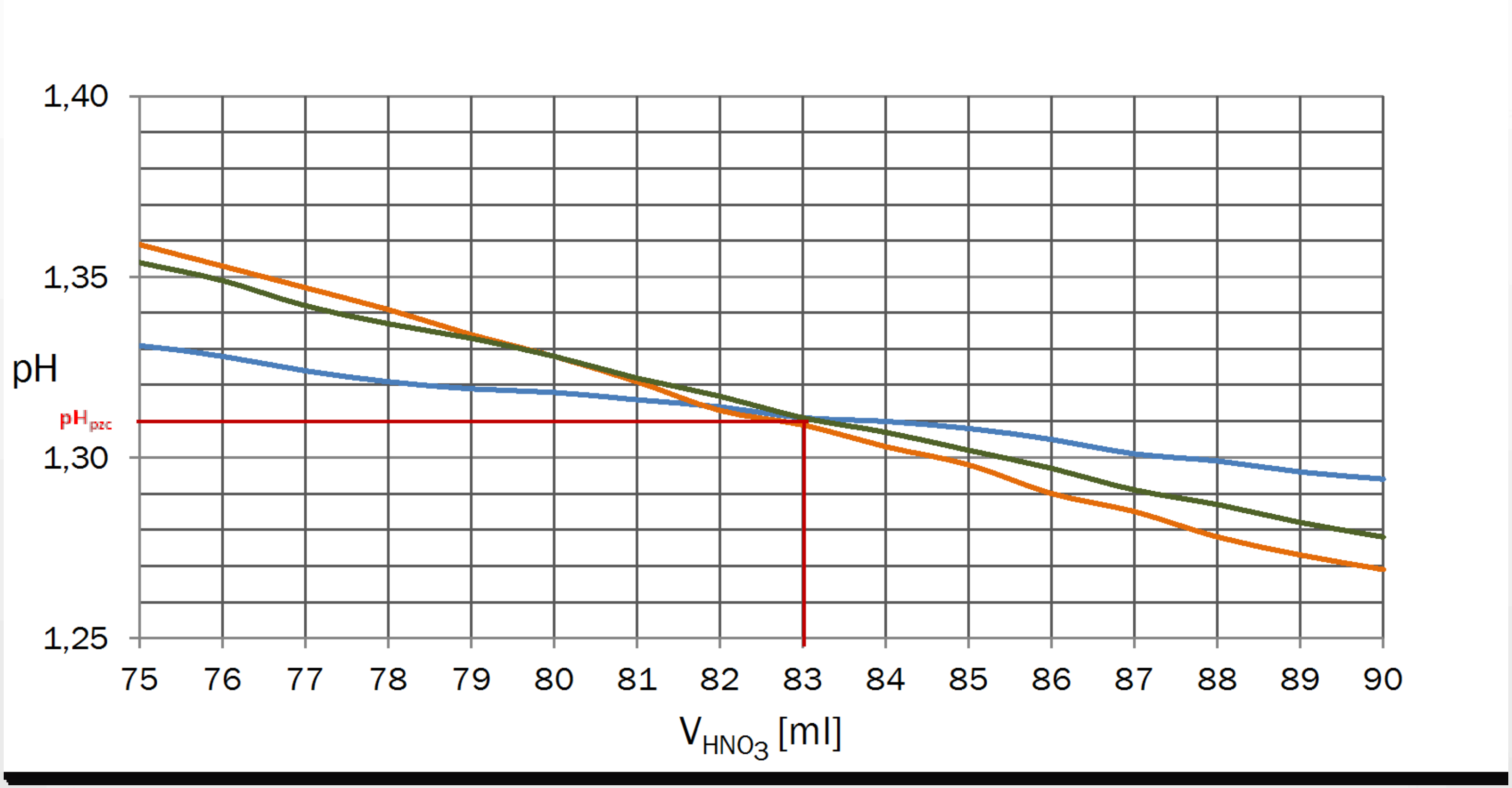
Nodules and Metals for E-mobility - LITHIUM



Titration curves for pH_{pZc} determination

[3] R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

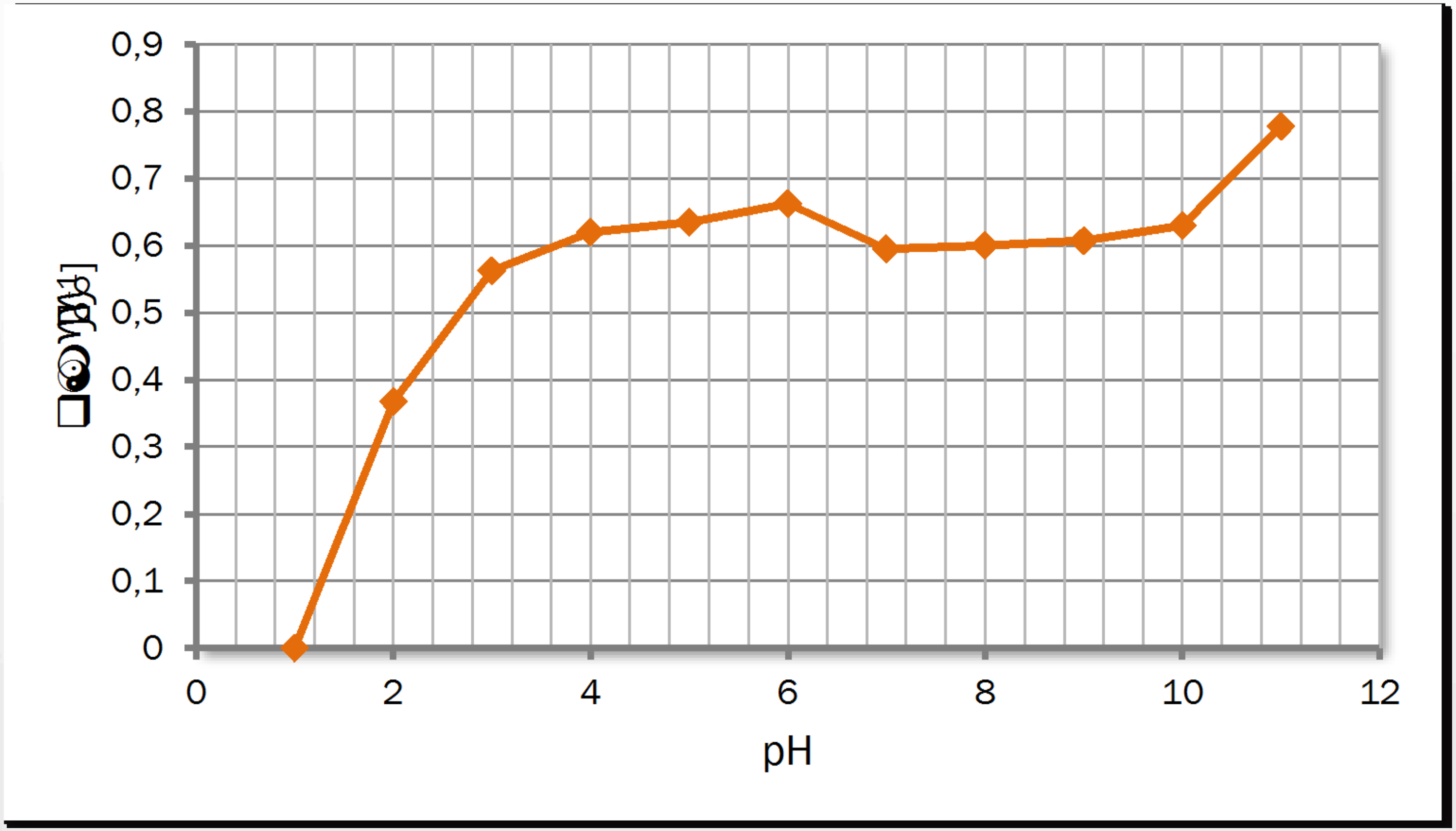
Nodules and Metals for E-mobility - LITHIUM



The point of zero charge pH_{pZc}

[3] R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

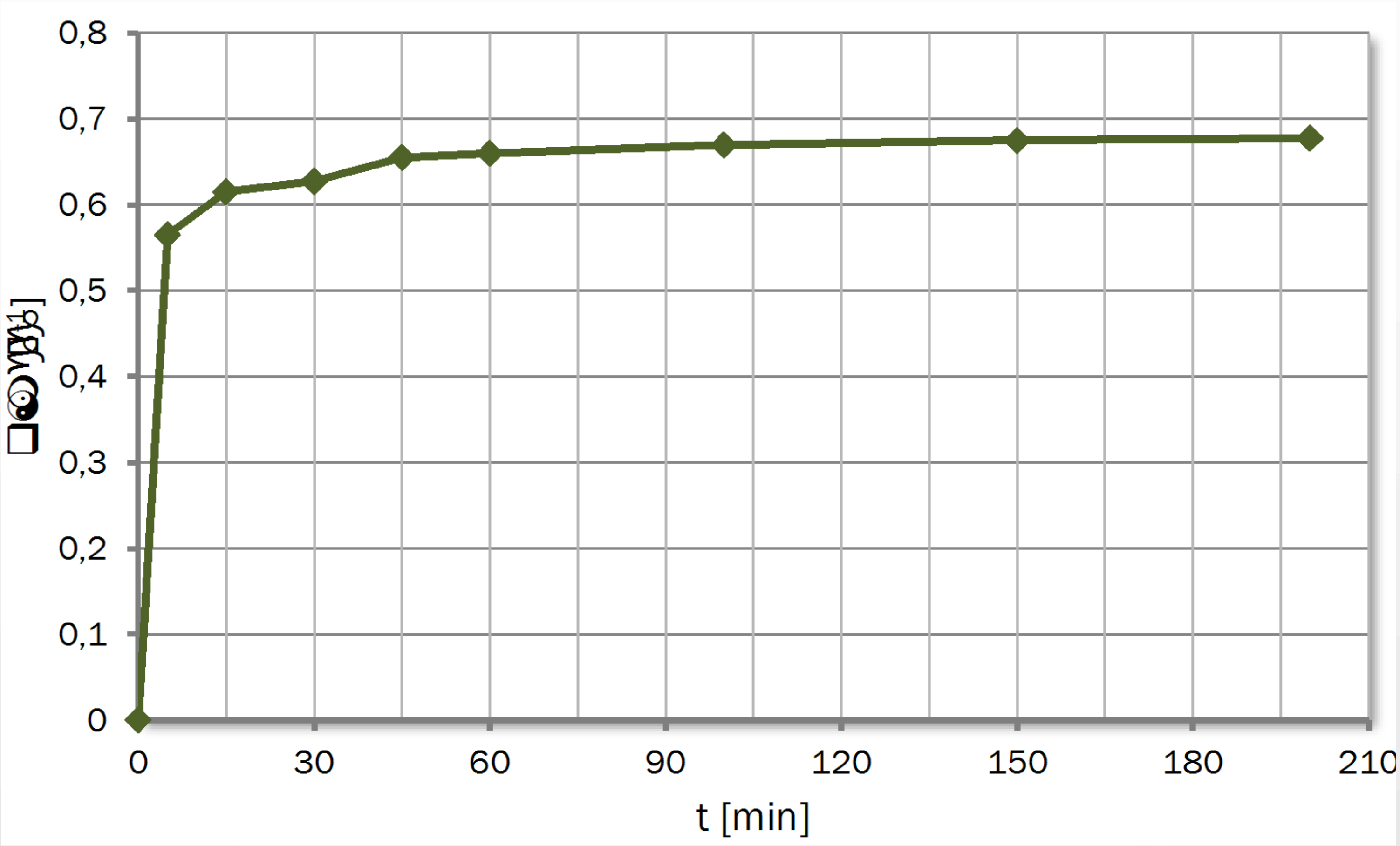
Nodules and Metals for E-mobility - LITHIUM



The dependence of the Li sorption capacity of the nodules on pH

[3]R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

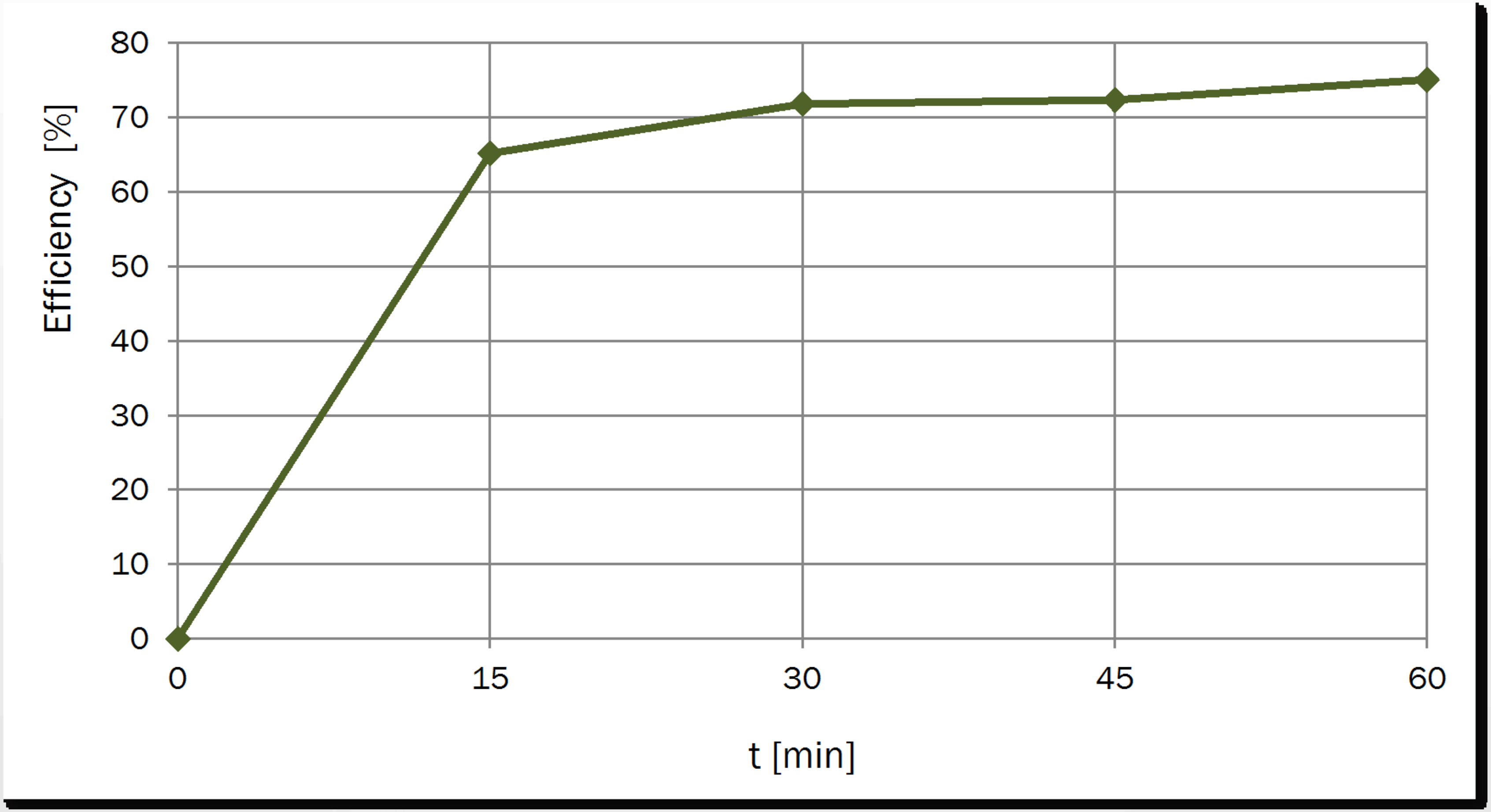
Nodules and Metals for E-mobility - LITHIUM



Li sorption kinetics of the untreated nodules, pH 4

[3] R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

Nodules and Metals for E-mobility - LITHIUM

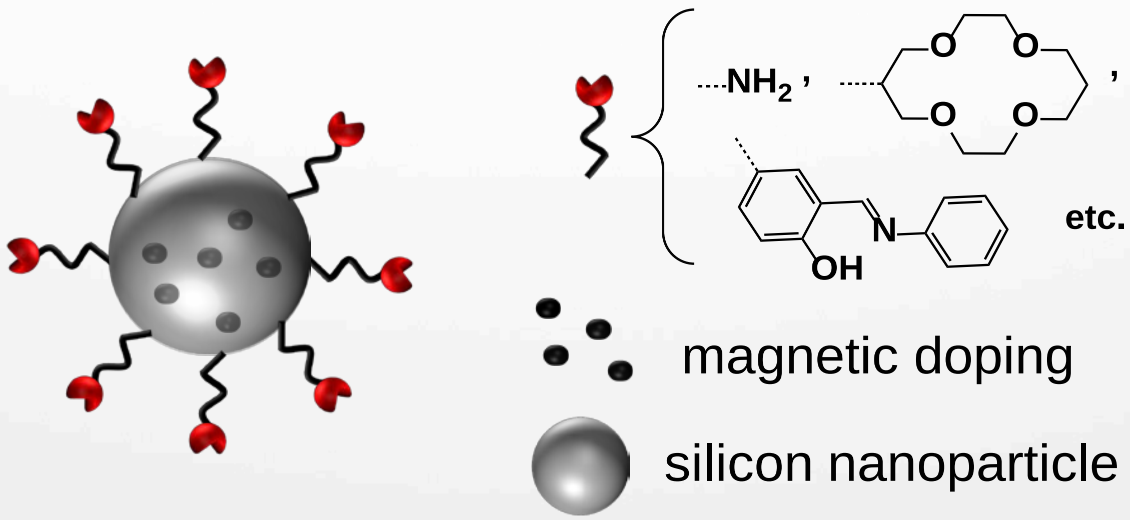


Desorption kinetics of Li from nodules, pH 1.2

[3] R. Hein, K. Mizell, A. Koshinsky and T. Conrad, 2013

Nodules and Metals for E-mobility - LITHIUM

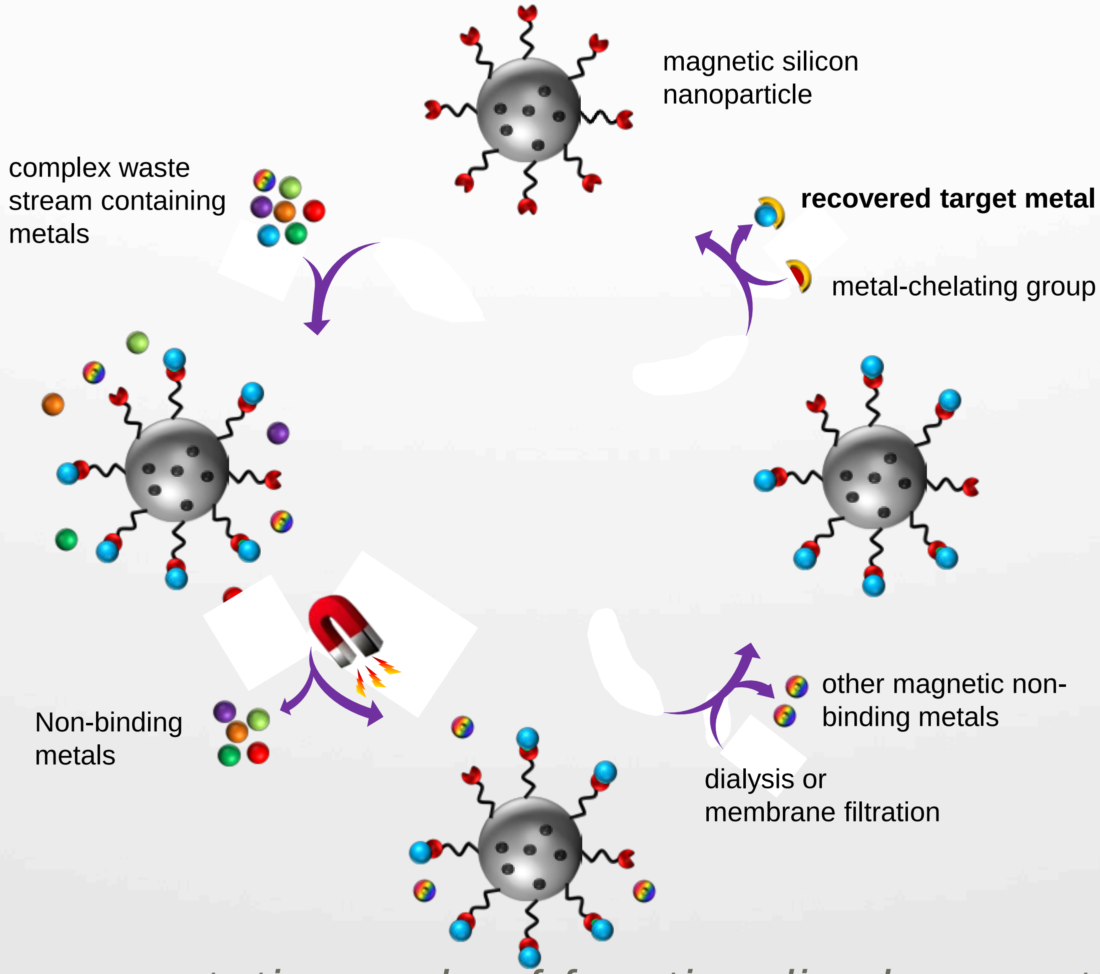
Another solution – a **new nano-adsorbent**



Synthesis of functionalized magnetic silicon-based nano-adsorbents

Nodules and Metals for E-mobility - LITHIUM

Another solution – a **new nano-adsorbent**



Schematic representation cycle of functionalized magnetic silicon-based nano-adsorbents process for metal recovery from leach solutions

Thank you