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

LUT
Lappeenranta
University of Technology

ON THE RECOVERY OF CAUSTIC AND ALUMINA FROM BAUXITE RESIDUES BY LEACHING

Teemu Kinnarinen
Postdoctoral Researcher
LUT School of Engineering Science
Lappeenranta University of Technology, Finland

Bauxite Residue Valorisation and Best Practices Conference
Leuven, 6 October 2015

OUTLINE OF THE PRESENTATION

- Background
- Materials and methods
- Results
  - Effect of leaching on particle size
  - Reduction of pH when water is added
  - Dissolution of Na and Al
  - Dissolution of caustic compounds

BACKGROUND

- Over 3 billion tons of bauxite residues have been disposed of in land deposits
- Leaching of various compounds occurs both in the disposal areas and in the washing process
- Recovery of Na, Al and caustic from the liquid phase is easier than recovery from the particle flocs
- In addition to the main compounds (Fe_2O_3, SiO_2, TiO_2, etc.), the flocs contain also Na, Al and caustic
- What is released from the flocs when the equilibrium is changed by adding water?

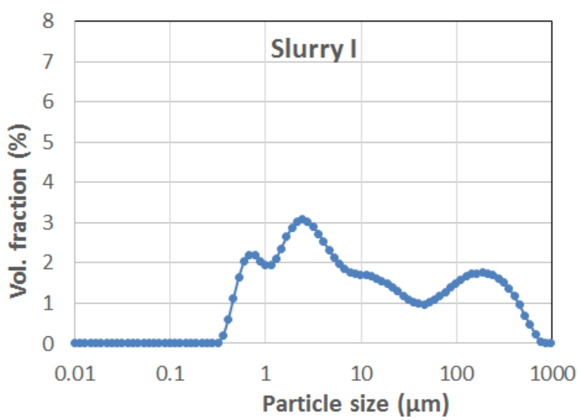
PROPERTIES OF SLURRY SAMPLES

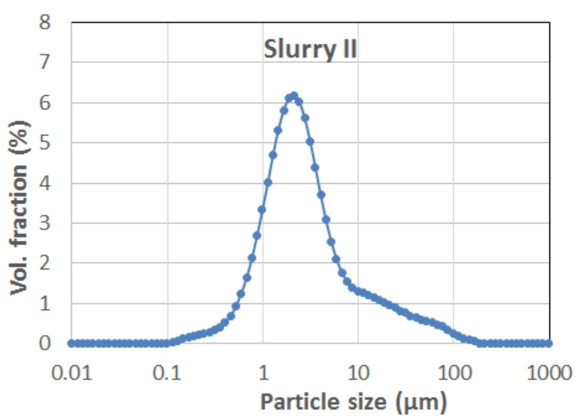
General properties

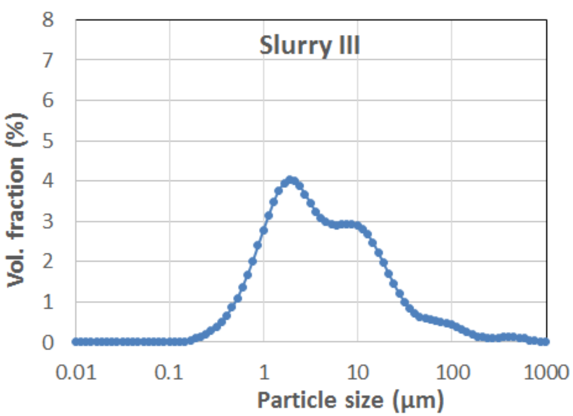
Slurry	pH (-)	TS* (g/kg)	TDS** (g/kg)	Density (kg/m³)	C_{Na}*** (g/kg)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
Slurry I	13.20	442	52	1363	27.2	0.87	6.9	235
Slurry II	12.92	330	8	1290	2.3	0.90	2.6	17
Slurry III	13.46	483	86	1450	33.3	0.90	3.9	27

*Total solids in slurry
**Total dissolved solids in the liquid phase of slurry
***Concentration of Na in the liquid phase of slurry

Particle size distributions







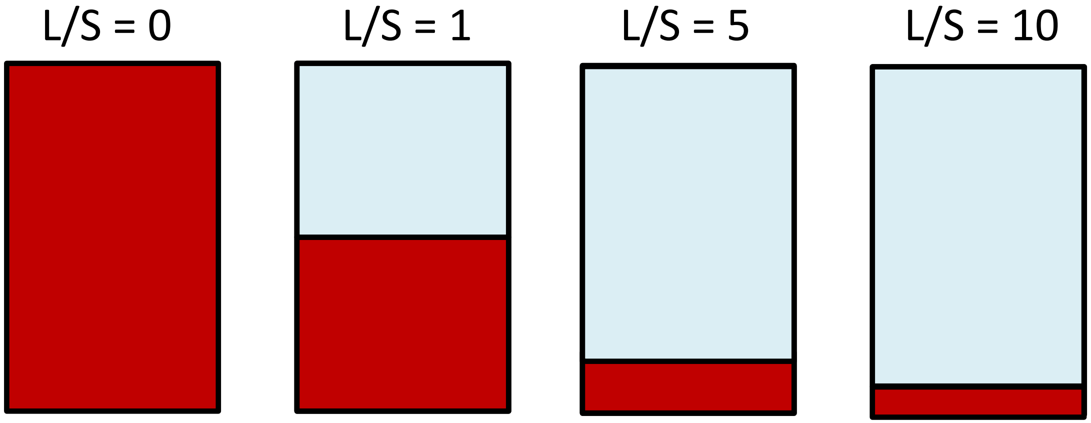
ELEMENTAL COMPOSITION OF SLURRIES

- Measured by a scanning electron microscope (SEM)
- The Ti and Ca concentrations were observed to vary significantly
- The low Na content of Slurry II is due to the dilute liquid phase

Slurry	C (w-%)	O (w-%)	Na (w-%)	Al (w-%)	Si (w-%)	Ca (w-%)	Ti (w-%)	Fe (w-%)
Slurry I	1	39	11	10	5	1	10	23
Slurry II	1	39	8	10	7	4	3	28
Slurry III	1	37	11	13	7	1	3	27

EXPERIMENTAL PROCEDURE

- Dilution of slurries with water
- Mixing of samples in orbital shaker
- Stabilization and settling in room temperature
- Measurement of particle size distributions
- Analysis of clear supernatant for Na with atomic absorption spectroscopy (AAS) by using two methods of sample preparation
- Analysis of clear supernatant for OH^- content with thermometric titration



THERMOMETRIC TITRATION

The main reactions

Step 1: Release of OH^- from aluminate

$$Al(OH)_4^- + n(C_4H_4O_6)^{2-} \rightarrow Al(OH)_3(C_4H_4O_6)_n^{2-} + OH^-$$

Step 2: Titration of free and released OH^- with HCl

$$H^+ + OH^- \leftrightarrow H_2O$$

Step 3: Titration of carbonate

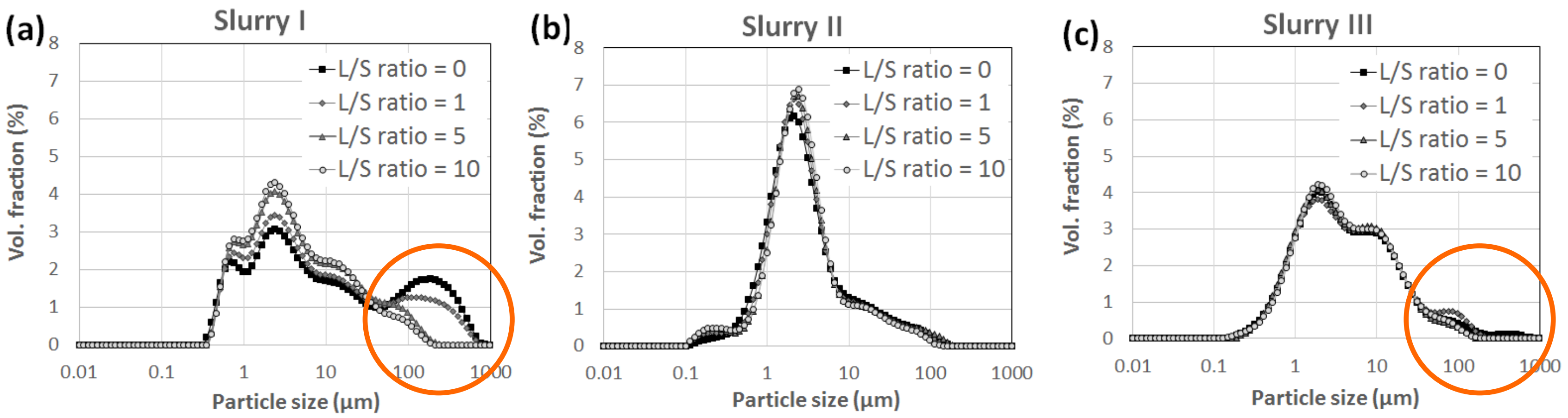
$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$$

Step 4: Determination of aluminum

$$Al(OH)_3(C_4H_4O_6)_n^{2-} + 6F^- \leftrightarrow 3OH^- + n(C_4H_4O_6)^{2-} + AlF_6^{3-} \downarrow$$

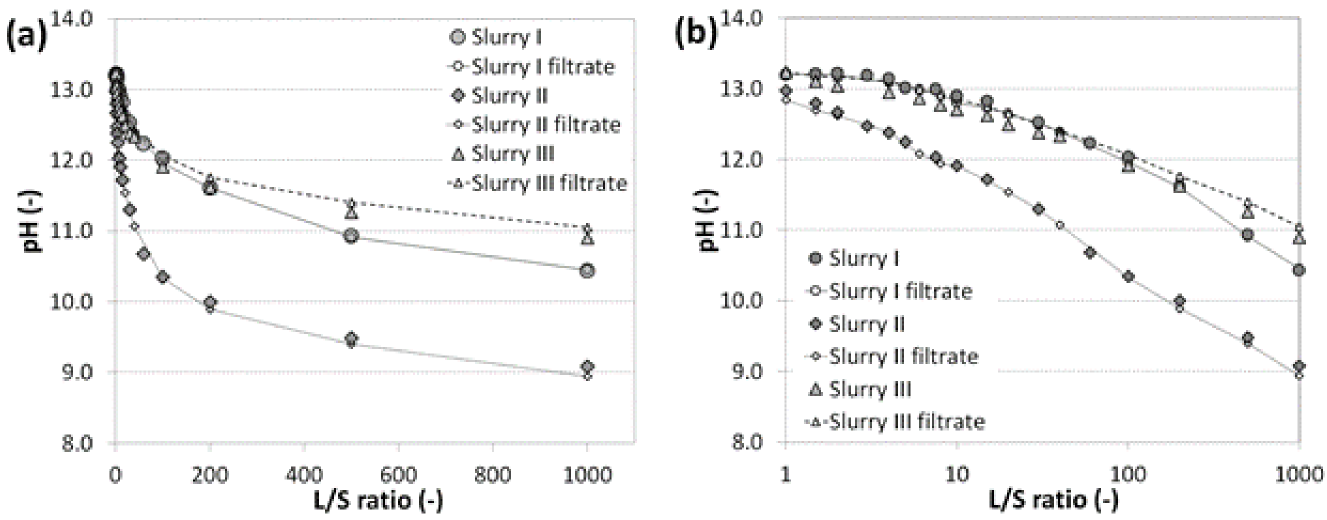
PARTICLE SIZE AFTER LEACHING

- Reduction of particle size may occur due to dissolution of particles or breakage of flocs
- The coarse end of the size distribution is more clearly affected
- The initial hydroxyl ion content seems to have an influence on the size reduction



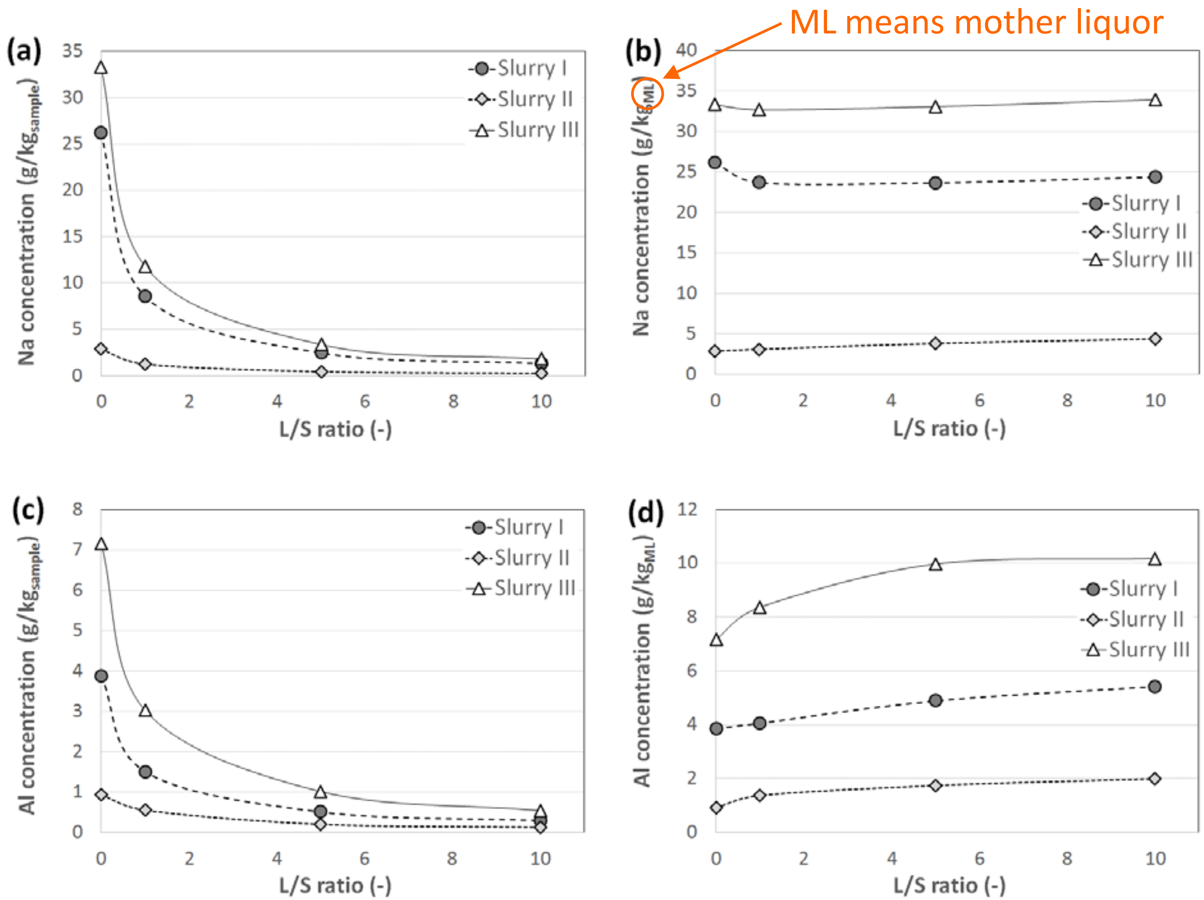
EFFECT OF L/S RATIO ON SLURRY pH

- The pH was measured after 15 min stabilization
- Large amounts of water are required to reduce the pH to below 11
- The obtained pH is not stable if suspended solids are present



DISSOLUTION OF SODIUM AND ALUMINUM

Dissolution results obtained with **water**



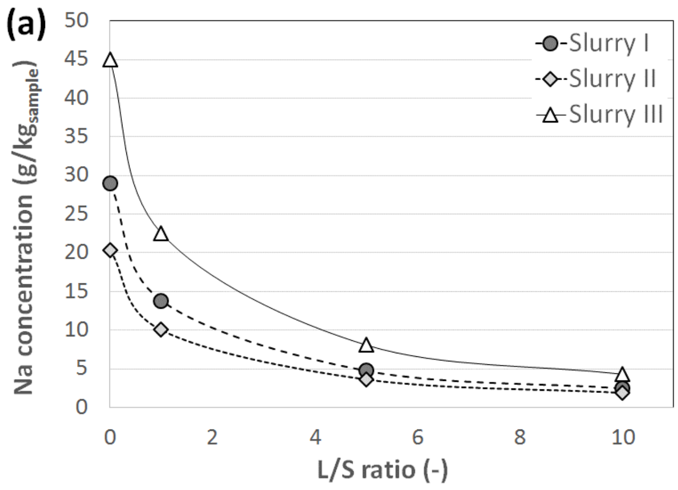
Na is not significantly dissolved in most cases

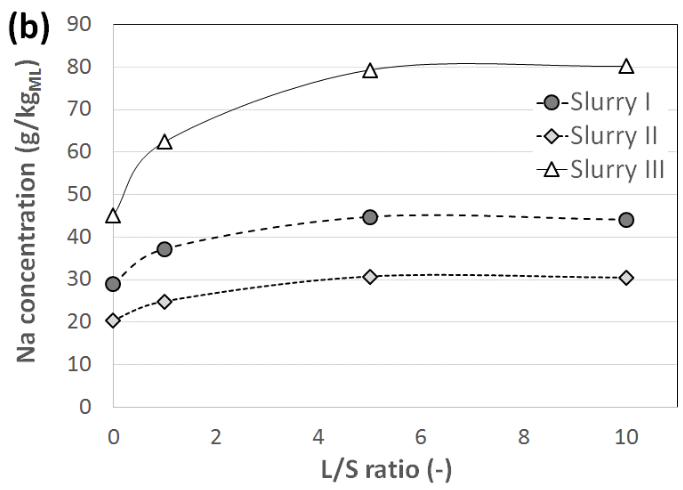
Al is liberated from solid particles

DISSOLUTION OF SODIUM

Dissolution results obtained with **nitric acid**

- Addition of nitric acid in the sample preparation stage
- A large amount of sodium is leached out from the solid phase





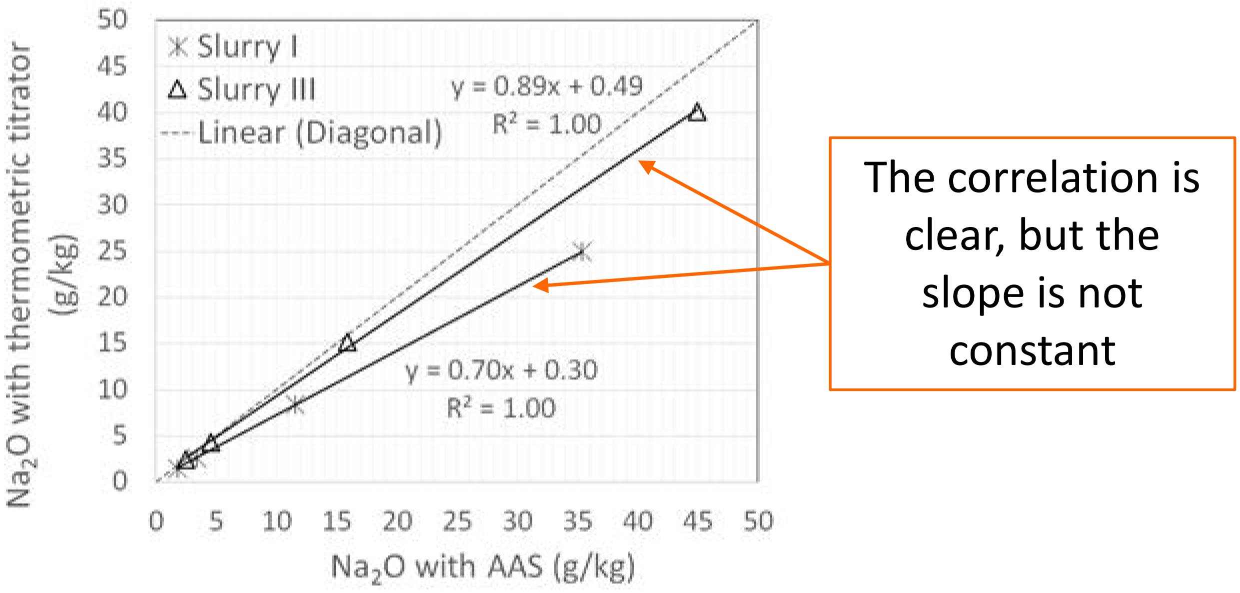
DISSOLUTION OF CAUSTIC COMPOUNDS

Total caustic = total hydroxyl ion (OH^-) content
= free hydroxyl ion content + 1 mol OH^- / 1 mol aluminate

- Most of total caustic is in the liquid phase
- Can we assume that the sodium concentration in the liquid phase represents the total caustic?
- How is the total caustic affected by addition of water?

DISSOLUTION OF CAUSTIC COMPOUNDS

- Correlation between Na_2O concentration measured with AAS and Na_2O concentration measured with thermometric titration



RELATIVE AMOUNTS OF THE COMPONENTS

Dilution increases →

Slurry #	Al/Na ratio (–)			
	$L/S^a = 0$	$L/S = 1$	$L/S = 5$	$L/S = 10$
Slurry I	0.15	0.18	0.21	0.22
Slurry II	0.33	0.44	0.45	0.47
Slurry III	0.21	0.26	0.30	0.30

[a] L/S means the mass ratio of added water and the original slurry.

The relative amount of Al increases with L/S ratio

Dilution increases →

Slurry #	Al/caustic ratio (–)			
	$L/S^a = 0$	$L/S = 1$	$L/S = 5$	$L/S = 10$
Slurry I	0.14	0.15	0.18	0.17
Slurry III	0.17	0.16	0.17	0.16

[a] L/S means the mass ratio of added water and the original slurry.

The effect of dilution on the Al/caustic ratio depends on the slurry

CONCLUSIONS

- The leaching behavior depends on the L/S ratio
- The slurry pH cannot be reduced by practically applicable amounts of water
- Aluminum is more readily leached with water
- A significant amount of sodium is dissolved when the pH is lowered with acid
- Each slurry behaves differently when diluted with water
- Effective separation techniques are required for improving the recovery of Na, Al and caustic

Thank you for
your attention!