# Hydrometallurgical processes at NTNU for sustainable production of feedstock for aluminum and solar industries

Jafar Safarian

4th Hydrometallurgy Seminar, March 6-7, 2018, Oslo

# **R**esurser, **E**nergi og **M**iljø (**REM**)

## Department of Materials Science and Engineering

## ❑ Who are we?

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Merete Tangstad

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Yongxiang Yang

# Research area

Metal production (Pyrometallurgy, Electrometallurgy, Hydrometallurgy)

Melt treatment

Energy supply and utilization

Recycling of metals

Environmental issues in metallurgical industry

Preparation and characterization of biomaterials

Raw Materials (ores, coals, …)

Refractory meterials ($SiO_2$, C, SiC, $Si_3N_4$, ..)

sfi Centre for Research-based Innovation

metal production

SUSOLTECH

The Norwegian Research Centre for Sustainable Solar Cell Technology

HighEFF

Centre for an Energy Efficient and Competitive Industry for the Future

MoZEES

Mobility Zero Emission Energy Systems

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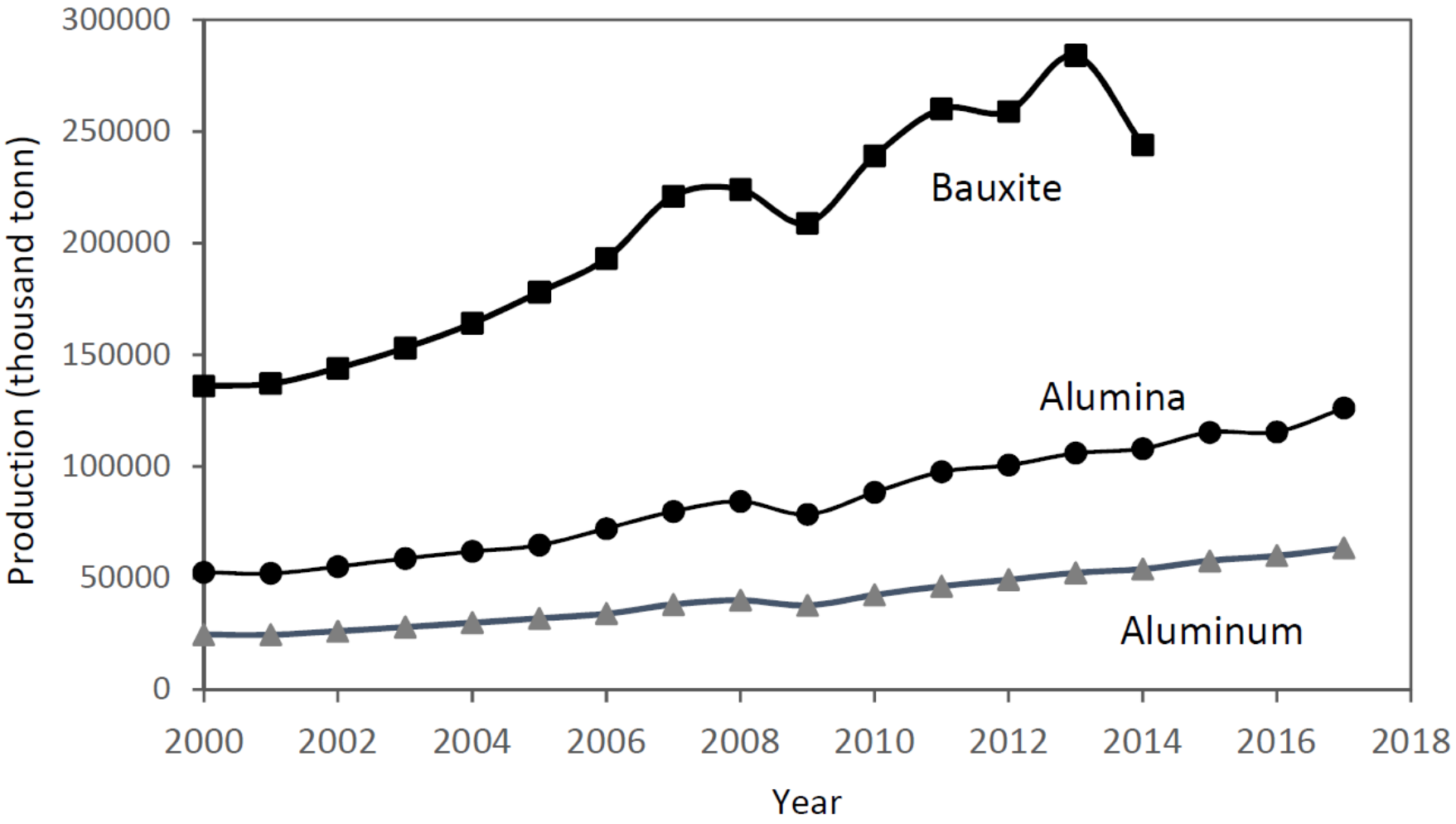
AMADEUS

ultra high temperature energy storage

ENSUREAL

SUSTAINABLE ALUMINA PRODUCTION

# Sustainable production of alumina



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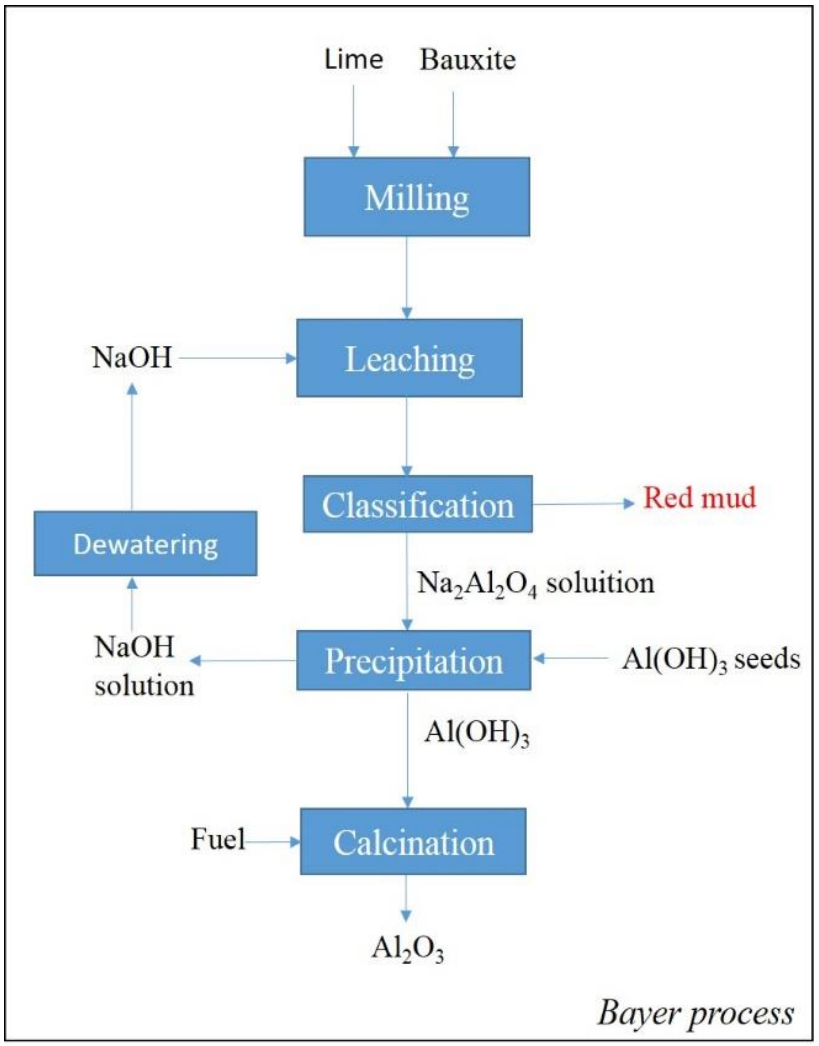
# Sustainable production of alumina

## Bayer process:



*Karl Josef Bayer (1847-1904)*

**Leaching:**

$Al(OH)_{3(s)} + NaOH \rightarrow NaAl(OH)_{4\ (aq)}$

$AlO(OH)_{\ (s)} + NaOH + H_2O \rightarrow NaAl(OH)_{4\ (aq)}$

**Precipitation:**

$NaAl(OH)_{4(aq)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)}$

**Calcination:**

$Al(OH)_{3(s)} \rightarrow Al_2O_{3\ (s)} + H_2O_{(q)}$

# Sustainable production of alumina

**Red mud:**

Table I: Chemical compositions of red mud produced from different bauxite sources in dry basis (wt%)

| Bauxite source | $Fe_2O_3$ | $Al_2O_3$ | CaO | $TiO_2$ | $Na_2O$ | $SiO_2$ |
|---|---|---|---|---|---|---|
| Greec[7,8,9] | 47.74 | 16.22 | 10.73 | 5.93 | 2.51 | 6.08 |
| | 44.6 | 23.6 | 11.2 | 5.7 | 2.5 | 10.2 |
| | 40.2 | 16.68 | 9.86 | 3.83 | 2.87 | 8.9 |
| India[6] | 35-37 | 18-21 | 2-3 | 17-19 | 5-6 | 6-7 |
| | 35-36 | 17-19 | 3-5 | 14-16 | 5-6 | 7-9 |
| | 44-46 | 19-21 | 1-2 | 17-19 | 3-4 | 5-7 |
| | 44-47 | 17-20 | 1-3 | 8-11 | 3-5 | 7-9 |
| | 40-46 | 18-22 | 1-3 | 3-4 | 4-5 | 12-16 |
| | 48-54 | 17-20 | 1-2 | 3-4 | 3-5 | 4-6 |
| Australia[10] | 28.5 | 24 | 5.26 | 3.11 | 3.4 | 18.8 |
| | 31.7 | 18.8 | 4.44 | 3.17 | 4.2 | 20.2 |
| | 29.6 | 17.3 | 3.64 | 2.65 | 3.2 | 30.0 |
| | 56.9 | 15.6 | 2.39 | 4.46 | 2.2 | 3.0 |
| | 34.8 | 23.2 | 2.25 | 8.03 | 7.1 | 9.2 |
| | 30.7 | 18.6 | 2.51 | 7.01 | 8.6 | 16.0 |
| Brazil[10] | 45.6 | 15.1 | 1.16 | 4.29 | 7.5 | 15.6 |
| Germay[10] | 44.8 | 16.2 | 5.22 | 12.33 | 4.0 | 5.4 |
| Spain[10] | 37.5 | 21.2 | 5.51 | 11.45 | 3.6 | 4.4 |
| USA[10] | 35.5 | 18.4 | 7.73 | 6.31 | 6.1 | 8.5 |
| Jamaica[11] | 42.3 | 16.4 | 9.1 | 6.0 | 4.6 | 8.0 |
| | 49.5 | 16.5 | 5.5 | 7.0 | 2.3 | 3.0 |

J. Safarian, L. Kolbeinsen: Sustainable Industrial Processing Summite & Exhibition, 06-10 November 2016, Hainan, China, pp. 75-82.

.

**Red mud formation causes direct loss of iron and aluminum oxides!**

# Sustainable production of alumina

## Red mud problem:

- Red mud is transported to holding ponds, usually close to the aluimna plant
- The stockpiling requires special procedures to minimize the risk of red mud flooding.
- Red mud has alkalinity and it requires neutralization to reduce its environmental impact; decreasing PH to lower acceptable levels is necessary.
  - Acid neutralization
  - $CO_2$ treatment,
  - Seawater neutralization
  - Bioleaching and sintering

**The Red Mud production indeed represents an environmental problem**

*Typical image of a red mud pond, Stade, Germany. (From Google.com/maps)*

# Sustainable production of alumina

Red mud catastrophe, Hungary, 2010.

Red mud catastrophe, Henan, China, 2016.

# Sustainable production of alumina

**Red mud problem:**

**Red mud:**

- **120 million t/y**
- **Around 3 billion tons worldwide**

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## Hydro is following orders of production cuts

**TOPICS:** Alunorte Brazil Norsk Hydro Norway Norway Today Pollution

Population in Belem, Para is concerned with the red mud flowing from the Hydro Alunorte compound, photo internet reproduction (Rio Times)

POSTED BY: PIETER WIJNEN 2. MARCH 2018

## Norsk Hydro is complying to production cuts in Brazil

**A court in Brazil has imposed Norsk Hydro's alumina refinery Alunorte production cuts of 50 per cent following accusations of contaminating the drinking water. the company state that they have complied too the requirement.**

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NORSK OLJEMUSEUM

RECENT NEWS

- Hydro is following orders of production cuts
- Elderly woman froze to death outside her flat
- Homeless people 'feel the breeze'
- SUPER COLD! Cold Snap Breaks Records

# Sustainable production of alumina

❖ Can we prevent the red mud production?

- ❖ A process was patented by **Harald Pedersen** in 1924.

- ❖ It was commercialized and had production of 17000 ton per year until 1969 in Høyanger, Norway. The process works for all kinds of ores, in particular for laterite.

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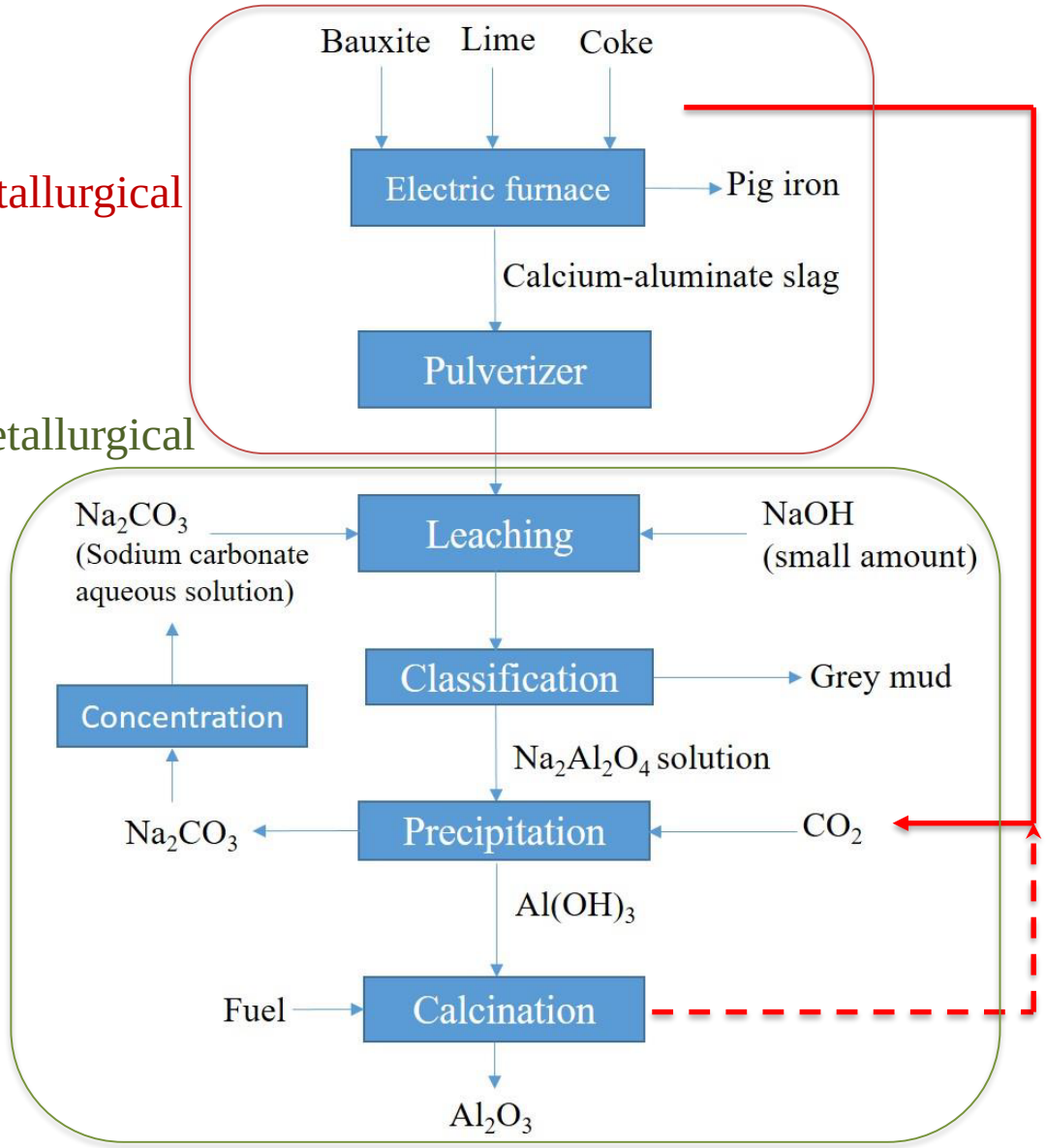
# Sustainable production of alumina

## Pedersen process:

Pyrometallurgical

Hydrometallurgical




$CO_2$

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metal production

www.ntnu.edu/web/metpro/about

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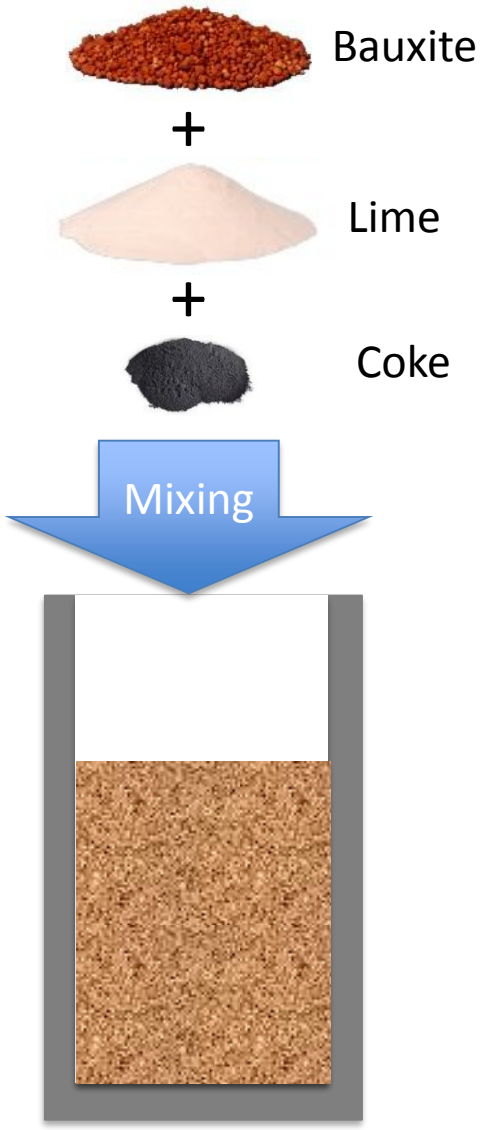
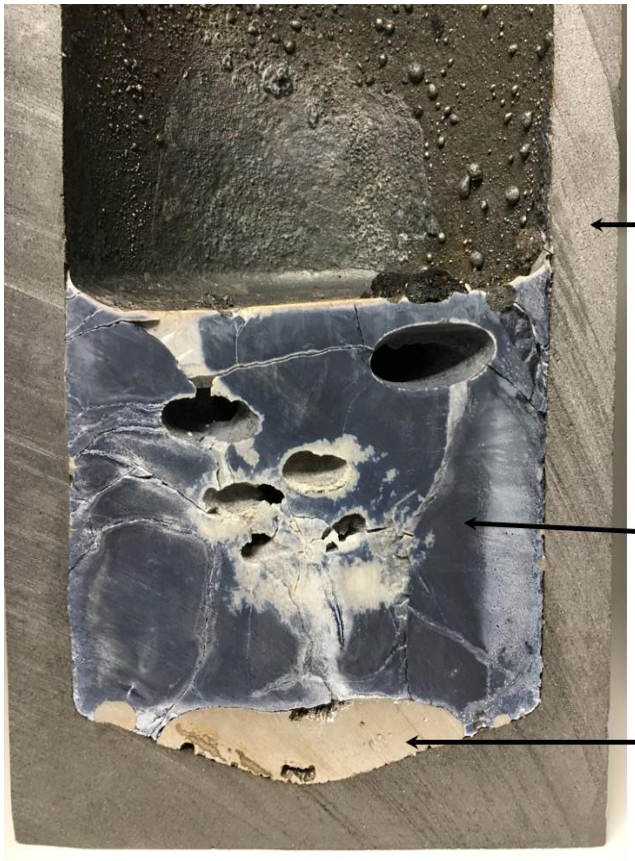
# Sustainable production of alumina

## Pyrometallurgical part:



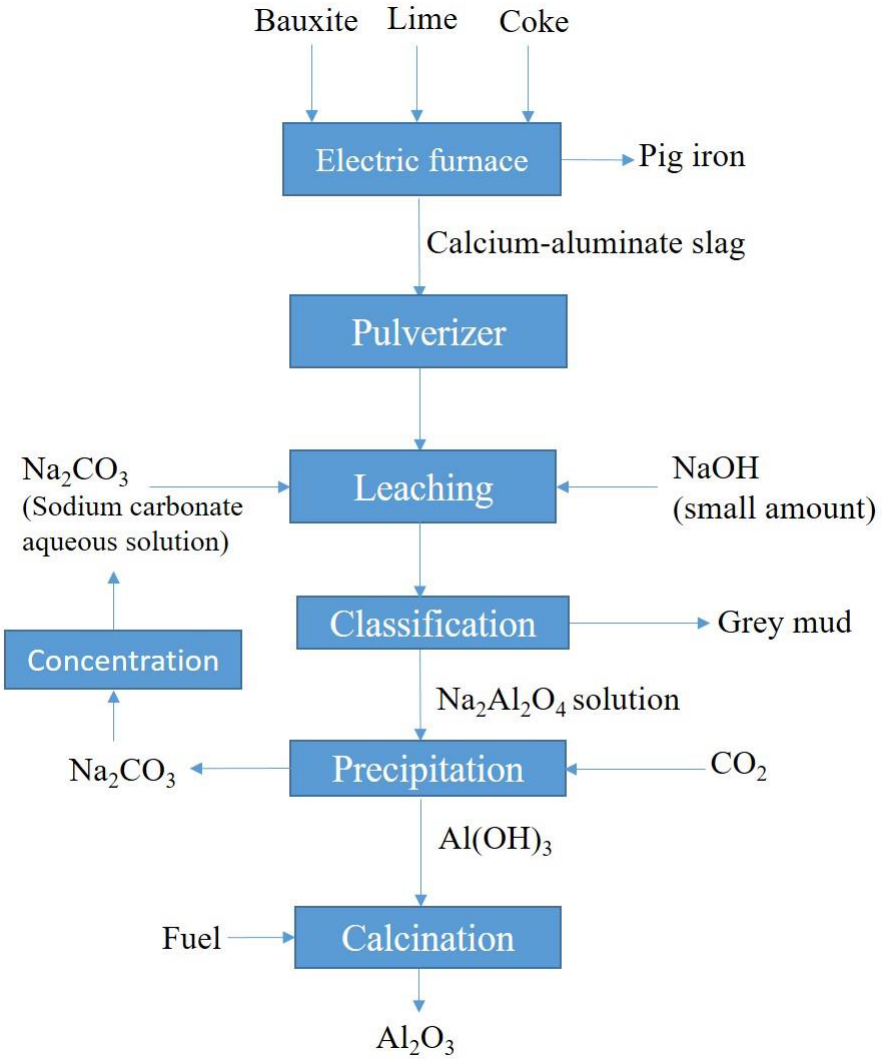




*Photograph: J. Safarian (unpublished work)*

Calcium-aluminate slag can be leached for alumina extraction

# Sustainable production of alumina

## Hydrometallurgical part:




**Leaching:**

$CaO \cdot Al_2O_3 + Na_2CO_3 \rightarrow 2\ NaAlO_2 + CaCO_3$

$12CaO \cdot 7Al_2O_3 + 12Na_2CO_3 \rightarrow 7\ NaAlO_2 + 12CaCO_3 + 10NaOH$

$3CaO \cdot Al_2O_3 + 3\ Na_2CO_3 \rightarrow 6\ NaAlO_2 + 3CaCO_3$ (<50%)

(40°C)

**Precipitation:**

$2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2\ Al(OH)_3 + Na_2CO_3$

(60 – 80°C)

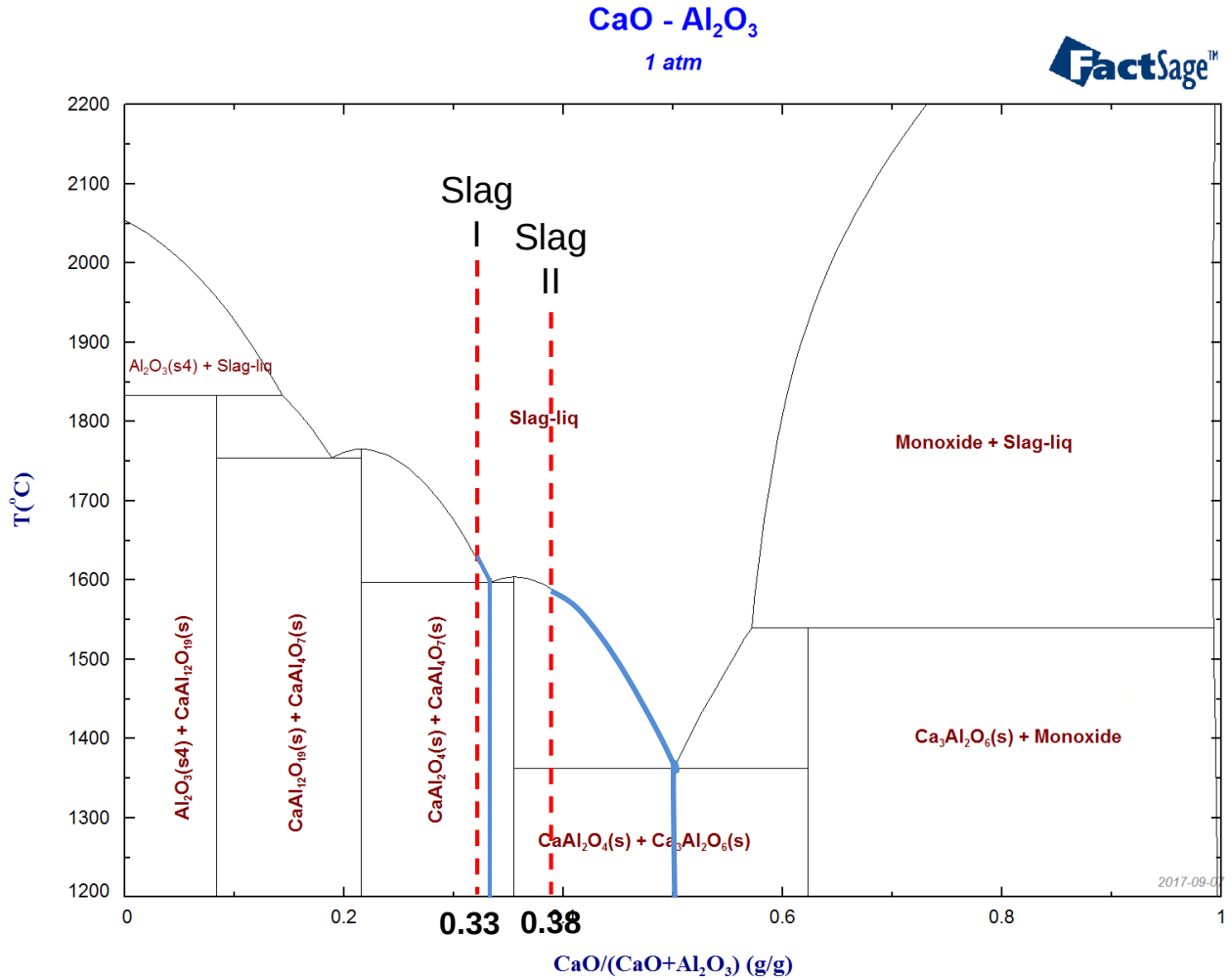
**Calcination:**

$Al(OH)_{3(s)} \rightarrow Al_2O_{3\,(s)} + H_2O_{(q)}$

J. Safarian, L. Kolbeinsen: Sustainable Industrial Processing Summite & Exhibition, 06-10 November 2016, Hainan, China.

# Sustainable production of alumina

## Typical slag leaching trials



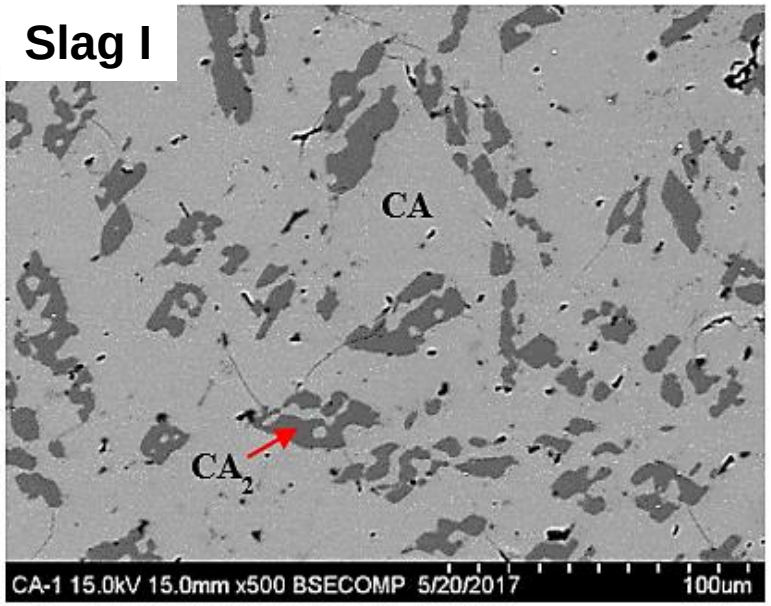

F. I. Azof et al.: Travaux 46, Proceedings of 35th International ICSOBA Conference, Hamburg, Germany, 2 – 5 October, 2017.

# Sustainable production of alumina

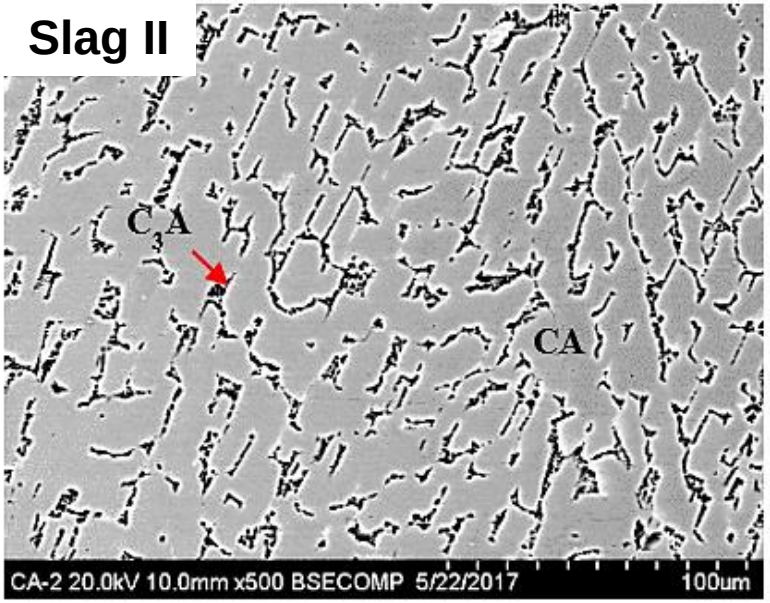
**Composition of Slags**

| Name | CaO (wt.%) | $Al_2O_3$ (wt.%) | CA phase (wt.%) | $CA_2$ phase (wt.%) | $C_3A$ phase (wt.%) |
|---|---|---|---|---|---|
| **Slag I** | 33 | 67 | 84 | 16 | - |
| **Slag II** | 38 | 62 | 91 | - | 9 |

**Slag I**




**Slag II**



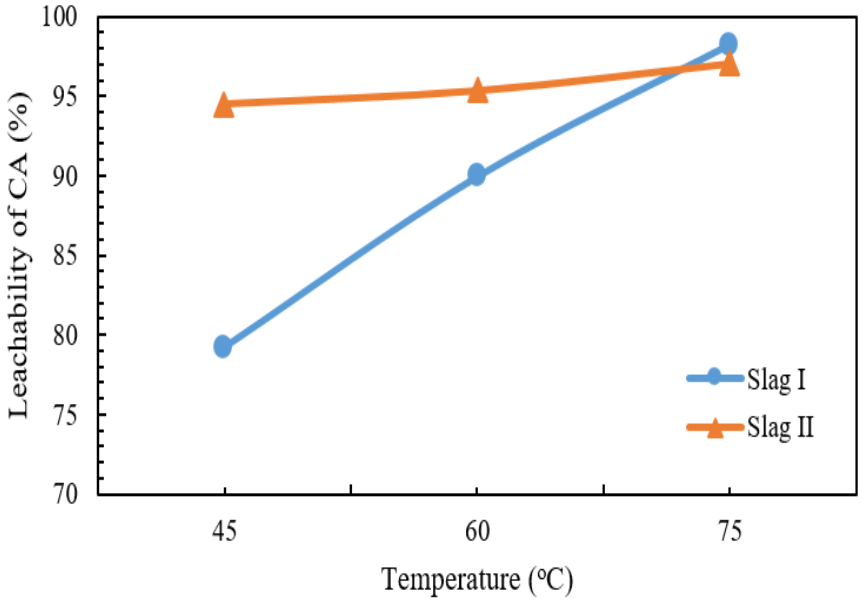

$CA = CaO.Al_2O_3$ ; $CA_2 = CaO.2Al_2O_3$ $C_3A = 3CaO.Al_2O_3$

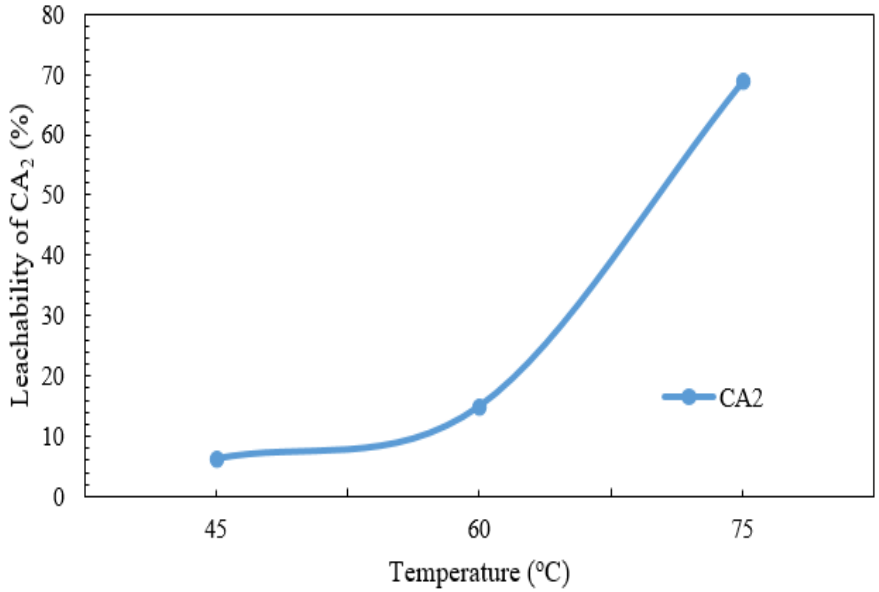
F. I. Azof et al.: Travaux 46, Proceedings of 35th International ICSOBA Conference, Hamburg, Germany, 2 – 5 October, 2017, pp. 243-254.

# Sustainable production of alumina

*Calculated semi-quantitatively

$$\eta_{leach} = \left( \frac{mass_{initial} - \left( wt.\%_{SQ} \times mass_{residue} \right)}{mass_{initial}} \right) \times 100\%$$

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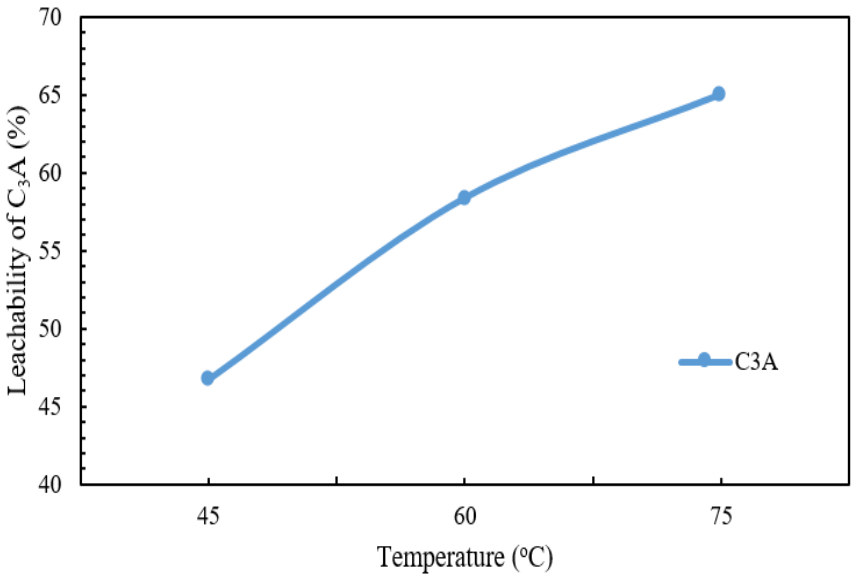
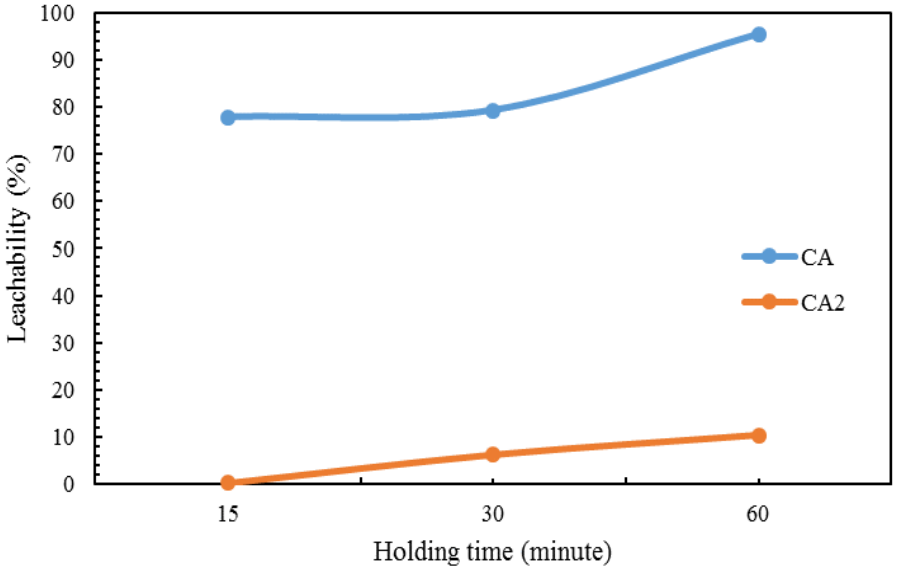
# Sustainable production of alumina




F. I. Azof et al.: Travaux 46, Proceedings of 35th International ICSOBA Conference, Hamburg, Germany, 2 – 5 October, 2017.

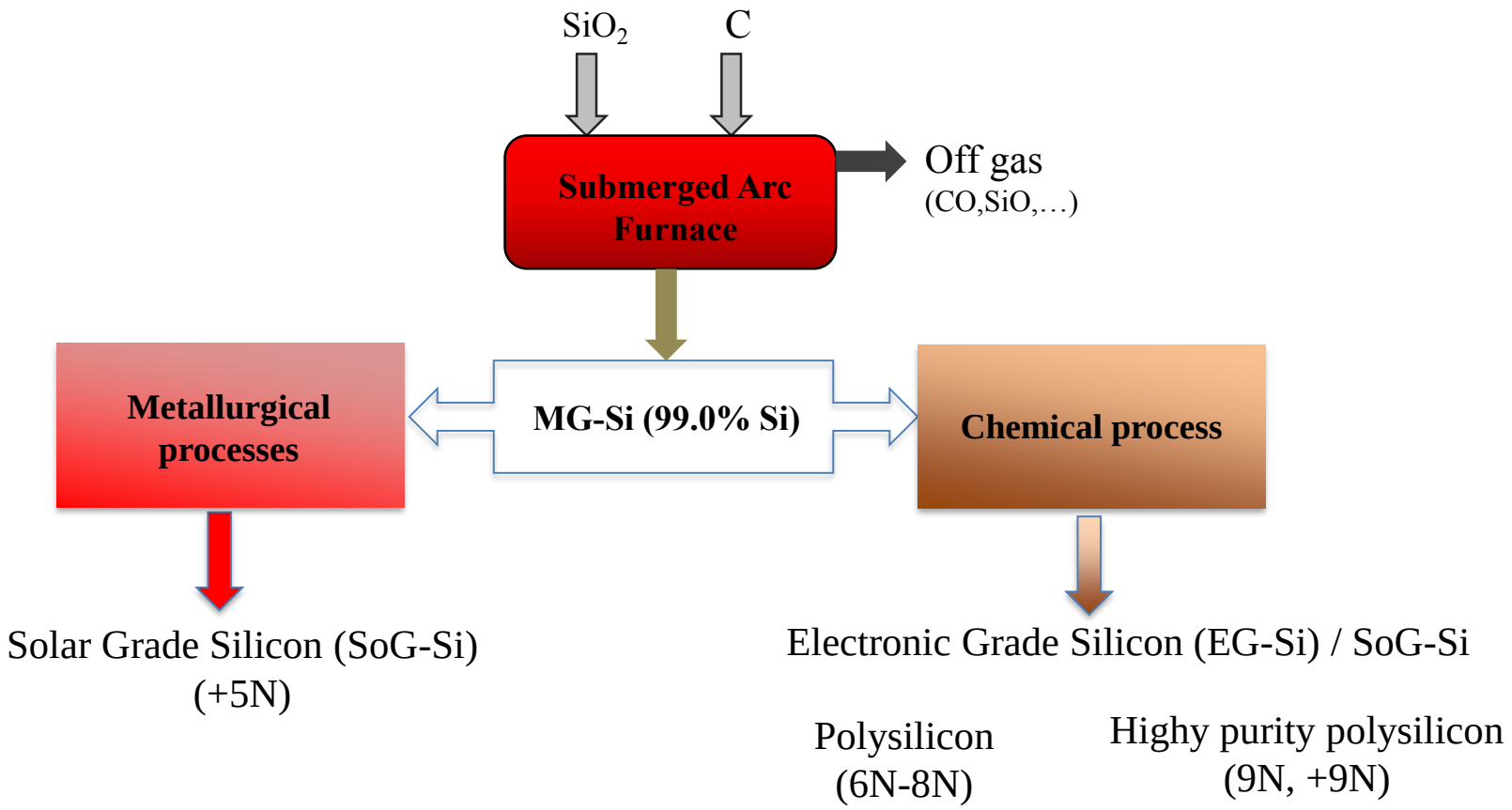
Leaching oven

# Sustainable production of alumina

**In ENSUREAL project:**

- The pyrometallurgical part of the Pedersen process
- The leachability of more binary and ternary slags is studied
- The leachability of slags produced through smelting-reduction of the bauxite ores is studied.
- The preicipitation of $Al(OH)_3$ from sodium-aluminate solutions is studied.
- Calcination of $Al(OH)_3$ to metallurgical grade alumina is studied.
- The whole process in pilot scale will be run through cooperation with SINTEF and other partners

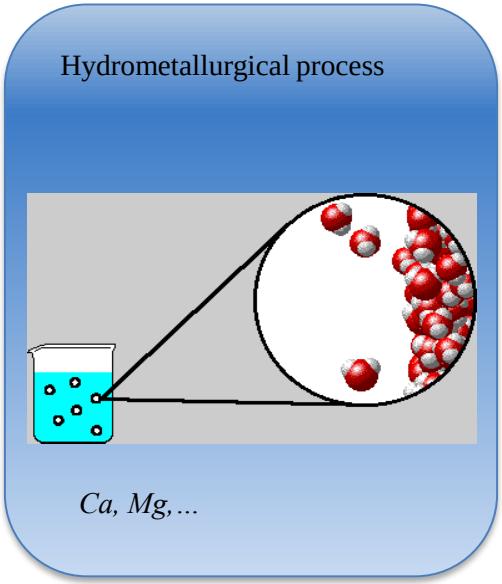
## Solar grade silicon feedstock production overview



## ELKEM Solar process

***Example:*** Acid leaching of silicon in ELKEM Soalr Process

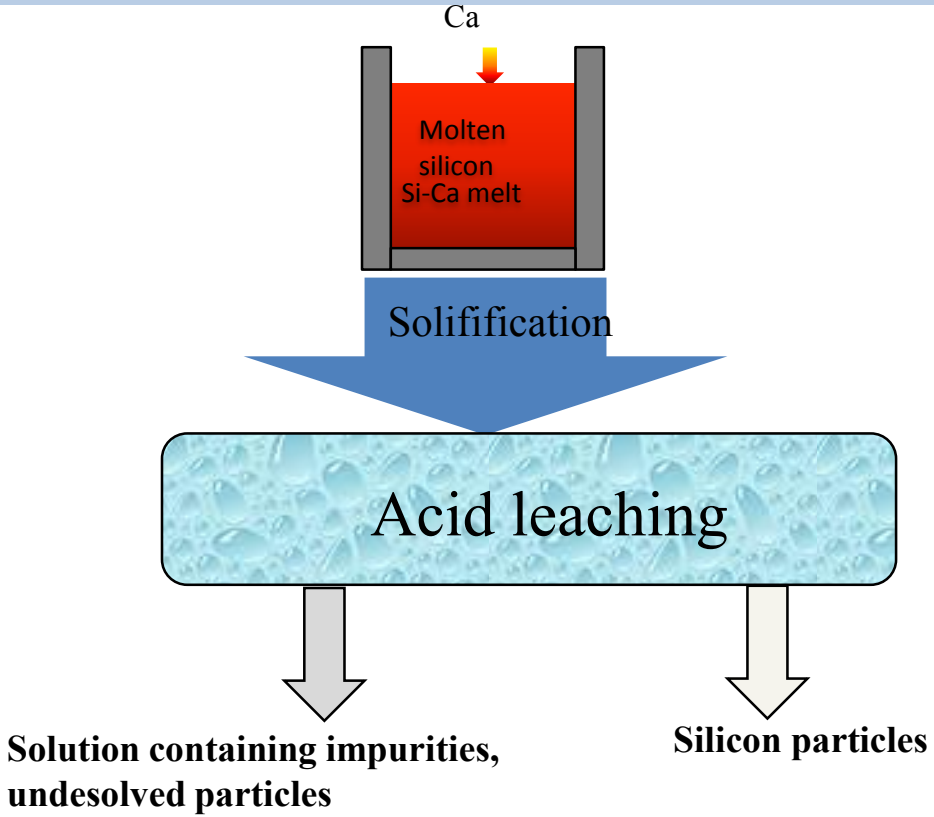
*Ref: www.elkem.com*




**In Acid leaching step:** The impurities are removed by acid leaching and the remained solid is silicon

# Sustainable production of solar silicon

## ❑ Silicon doping by Ca:




• When lumps of the alloy are treated with dilute HCl acid:

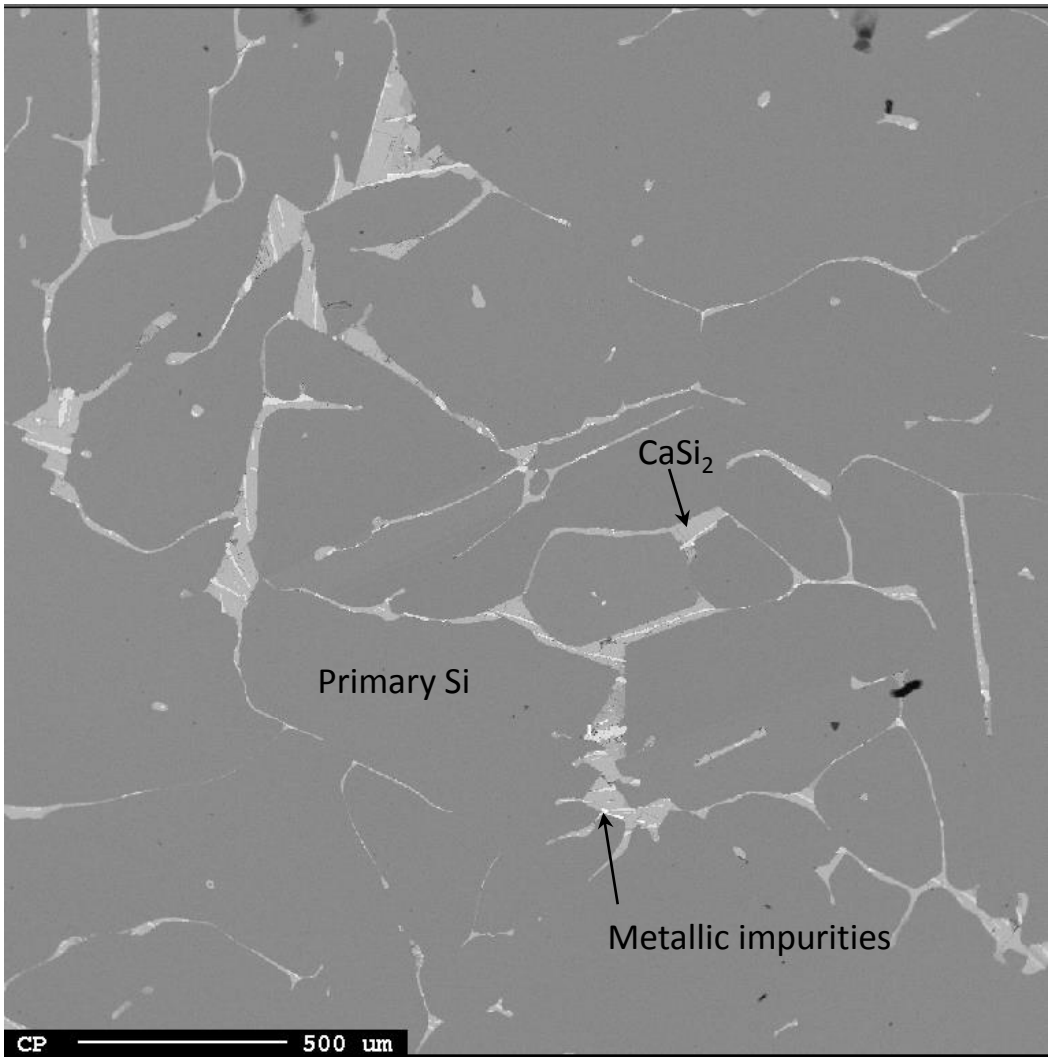
$$3CaSi_2 + 6HCl + 3H_2O = Si_6H_6O_{3(s)} + 3CaCl_2 + 3H_2$$

• The $CaSi_2$ swells and the lumps disintegrate to silicon grains around 1-2 mm

• The fine grained material containing impurities is easily separated from the silicon grains by washing.

# Sustainable production of solar silicon

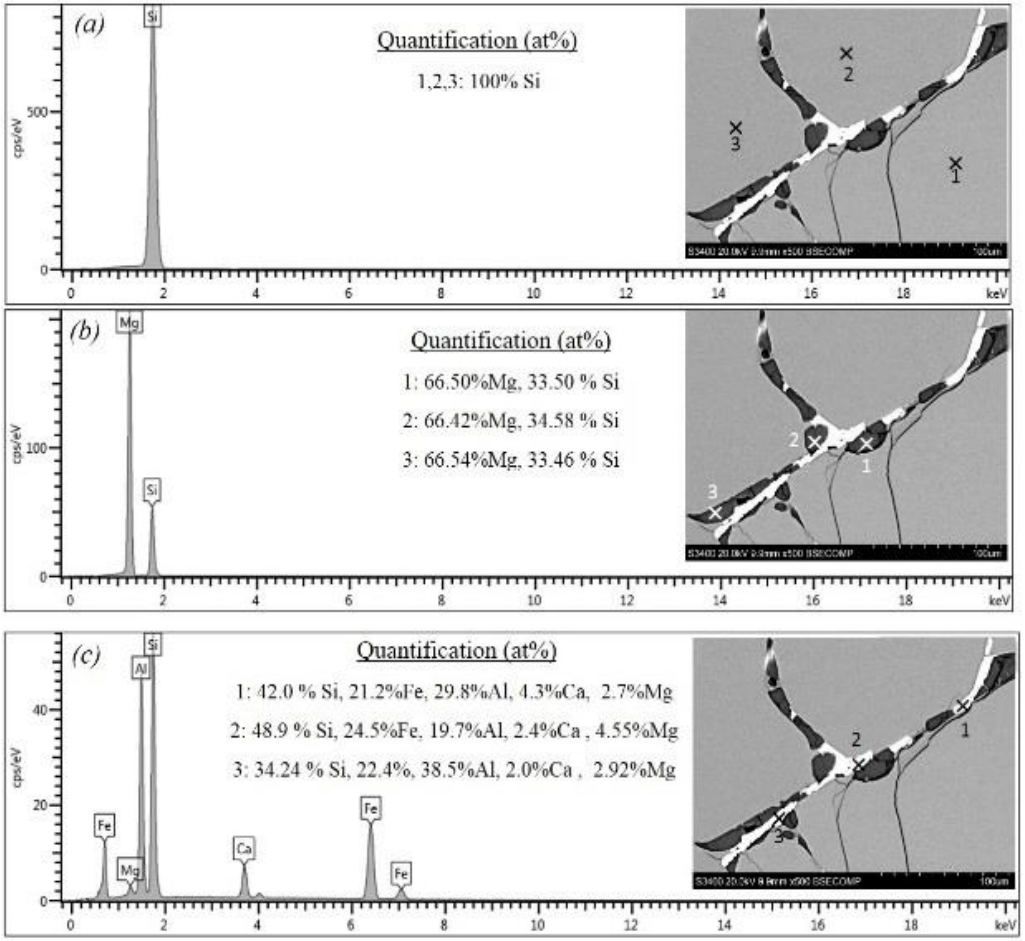
*Microstructure of a Si-4wt%Ca alloy containing metallic impurities*




*Scanning electron micrograph: J. Safarian (unpublished work)*

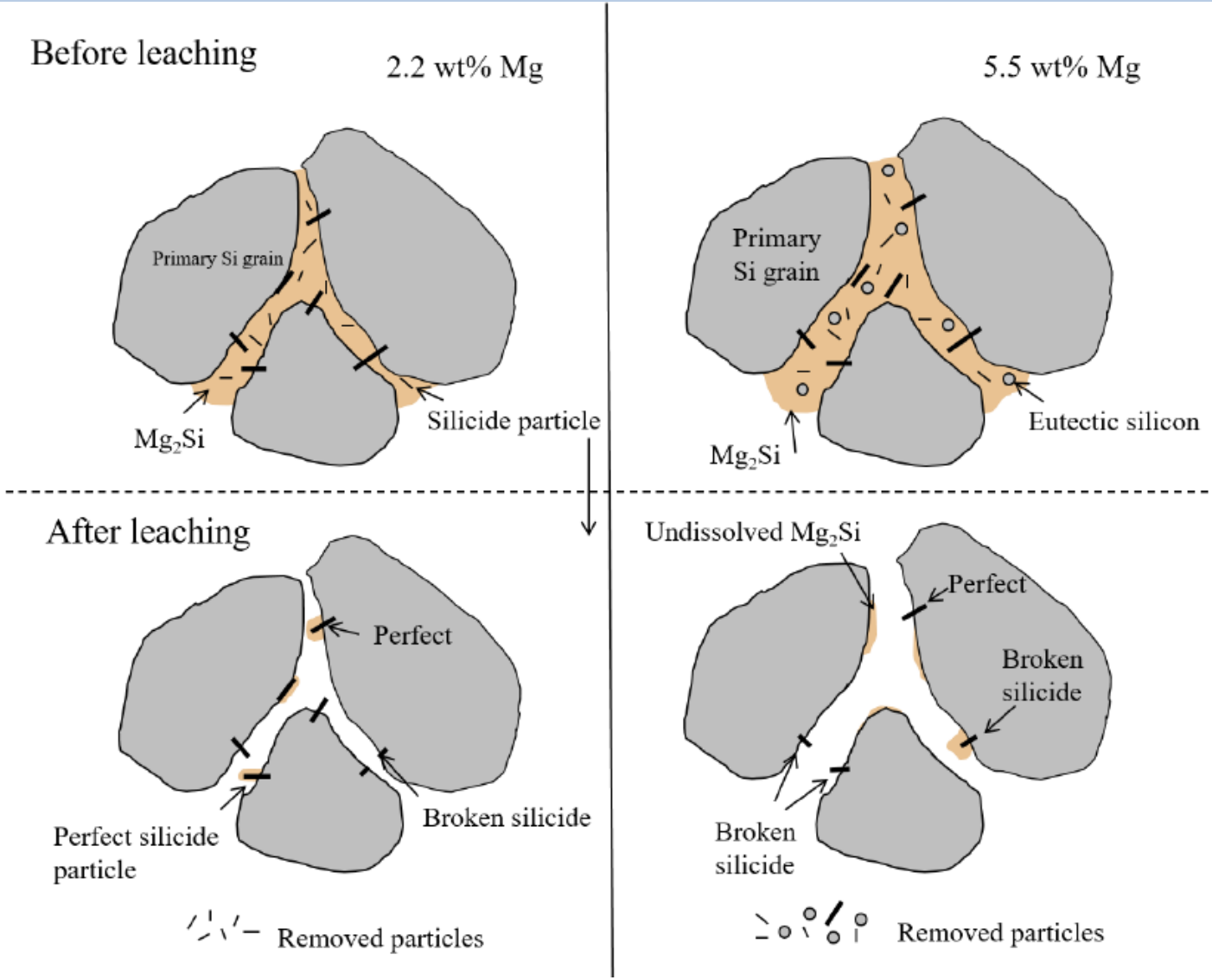
# Sustainable production of solar silicon

## ❑ Silicon doping by Mg:




*J. Safarian et al. 32nd European Photovoltaic Solar Energy Conference and Exhibition, 2016, Munic, Germany, pp.1011-1014.*

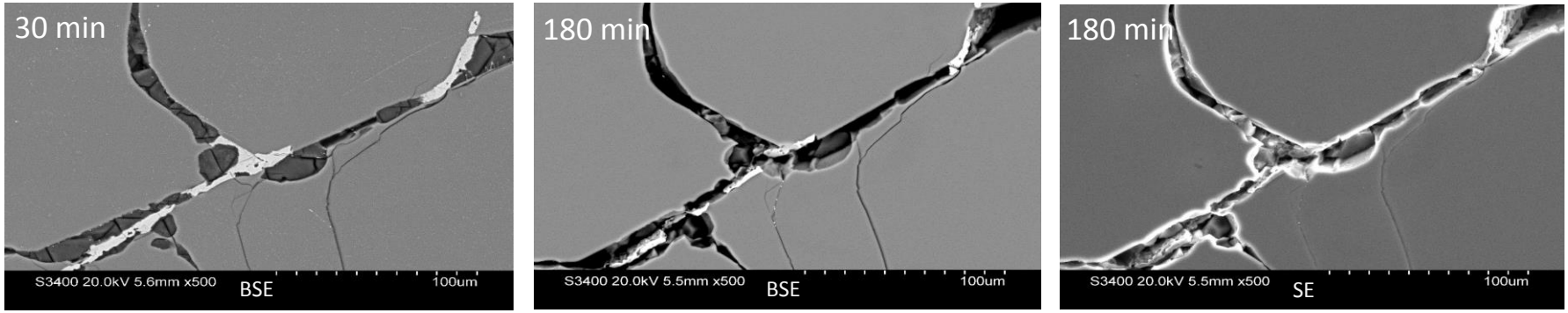
# Sustainable production of solar silicon




*S. Espelien, J. Safarian: AIMS Energy, 5(4): pp. 636-651.*

# Sustainable production of solar silicon

What happens when $Mg_2Si$ phase is leached?




Secondary Electron (SE) and BSE images of silicon sample containing 2.1wt% Mg at different leaching durations.

*J. Safarian et al. 32nd European Photovoltaic Solar Energy Conference and Exhibition, 2016, Munic, Germany, pp. 1011-1014.*

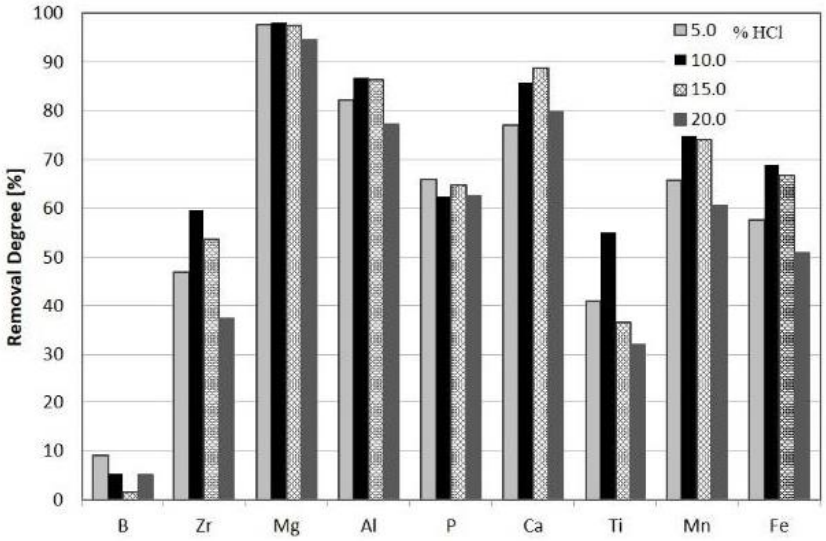
**Mg use as the refiner metal:**

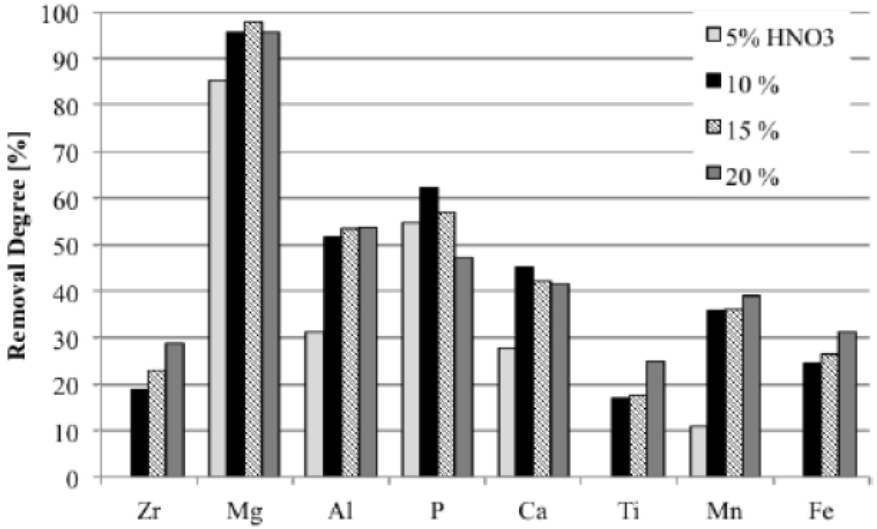
- Low silicon loss
- Low energy consumption process
- Sustainable approach

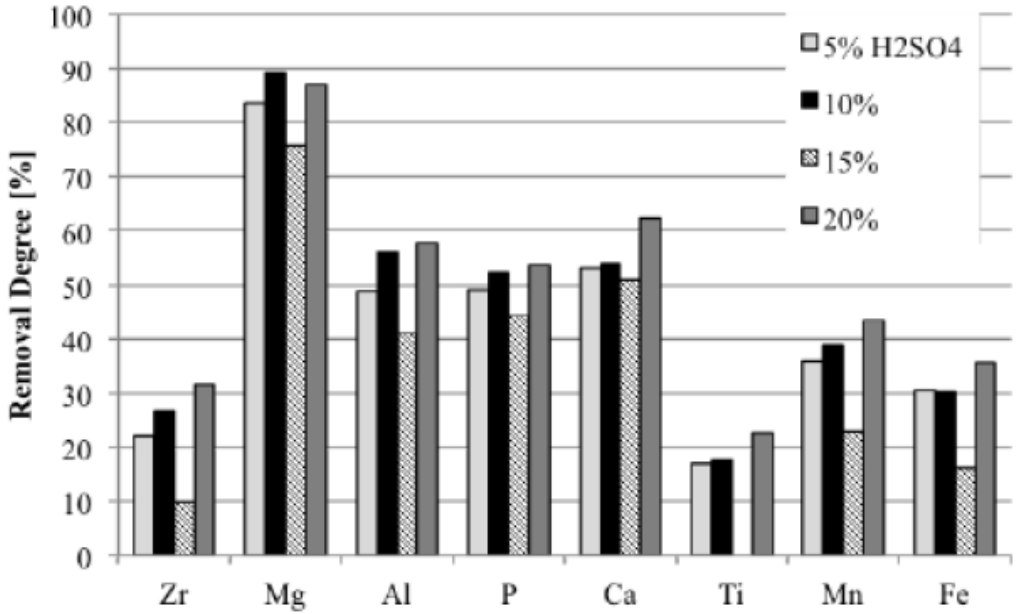
SUSOLTECH

The Norwegian Research Centre for Sustainable Solar Cell Technology

# Sustainable production of solar silicon




*J. Safarian et al. 33nd European Photovoltaic Solar Energy Conference and Exhibition, 2017, Amsterdam, Nederland, pp. 476-470.*



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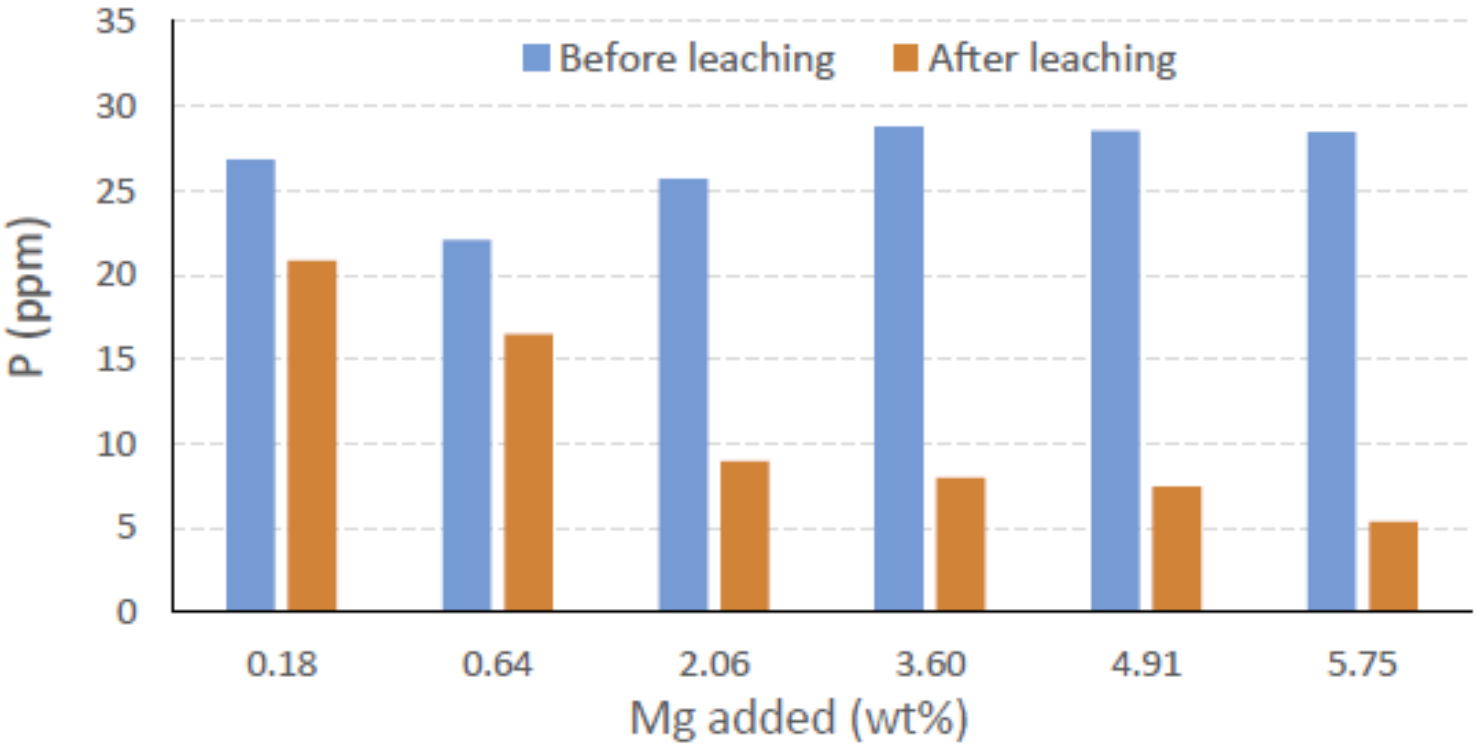
# Sustainable production of solar silicon




Leaching by 15%HCl at 80°C for 3 hours, and then by 2.5%HCl at 80°C for 3 hours.

*J. Safarian et al. 32nd European Photovoltaic Solar Energy Conference and Exhibition, 2016, Munic, Germany, pp.1011-1014.*

## ❑ Summary:

- Sustainable alumina production
- Sustainable production of Alumina through pyrometallurgical-Hydrometallurgical approach is possible and can solve the red mud problem
- Reviving the Pedersen process is a proper approach; ENSUREAL project goal is demonstration of a modernized Pedersen process in TRL 7.
- Knowledge-building about the hydrometallurgical Pedersen process is necessary

- Sustainable Solar silicon production
- Acid leaching process for solar silicon production is very effective
- Application of Mg as a refiner metal is a sustainable approach
- The acid leaching of Mg-doped silicon is effective to remove many impurities, in particular phosphorus

# References:


- F. I. Azof, L. Kolbeinsen, J. Safarian: The leachability of calcium aluminate phases in slags for the extraction of alumina, Travaux 46, Proceedings of 35th International ICSOBA Conference, Hamburg, Germany, 2 – 5 October, 2017, pp. 243-254.
- H. Sellæg, L. Kolbeinsen, J. Safarian: *Iron separation from bauxite through smelting-reduction process*, Light Metals Symposium 2017, San Diego, CA, February 26th 2017, pp. 127-135.
- J. Safarian, L. Kolbeinsen: *Sustainability in alumina production from bauxite*, 2016-Sustainable Industrial Processing Summite & Exhibition, 06-10 November 2016, Hainan, China, pp. 75-82.
- J. Safarian, L. Kolbeinsen: *Smelting-reduction of bauxite for sustainable alumina production*, 2016-Sustainable Industrial Processing Summit & Exhibition, 06-10 November 2016, Hainan, China, pp. 149-158.
- S. Espelien, J. Safarian: Effect of acid leaching conditions on impurity removal from silicon doped by magnesium, AIMS Energy, 2017, 5 (4): 636-651.
- S. Espelien, G. Tranell, J. Safarian: Effect of magnesium addition on removal of impurities from silicon by hydrometallurgical treatment, Energy Technology 2017, San Diego, CA, February 26th, pp. 355-365.
- J. Safarian, G. Tranell: *Silicon purification through magnesium addition and acid leaching*, 32nd European Photovoltaic Solar Energy Conference and Exhibition, 20-24 June 2016, Munic, Germany, pp.1011-1014.

# Thank you for your attention!