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# By-products valorisation in sulfobelite cements

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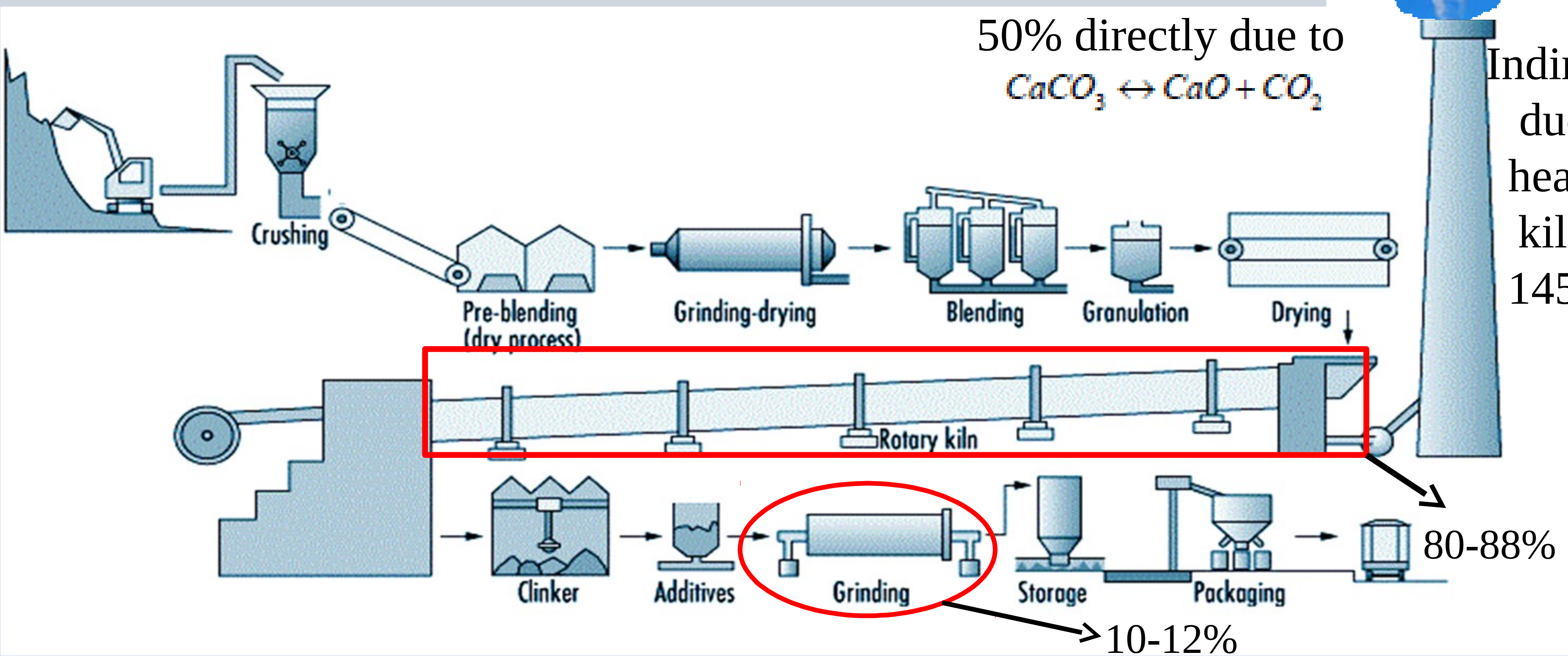
# Industrial Production

$900 kg\ CO_2/t$ cement

Global Production 4.8 Gt/y
Energy consumption 480 EJ/y

50% directly due to
$CaCO_3 \leftrightarrow CaO + CO_2$

Indirectly due to heating kiln at 1450°C




80-88%

10-12%



Prodan L., Bachofen G., “Encyclopedia of Occupational Health and Safety”, Chapt.93, International Labour Office, 1998.

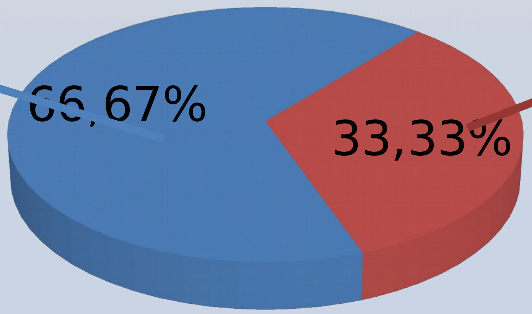
# Cement

- Hydraulic inorganic binder material
- Interconnects aggregates (gravel, sand) → concrete

**Cement** = Clinker + Gypsum (+Additives)

**OPC Clinker**

**Early strengths**




**Later strengths**

alite $(CaO)_3SiO_2$

belite $(CaO)_2SiO_2$

$$CaCO_3 \leftrightarrow CaO + CO_2$$

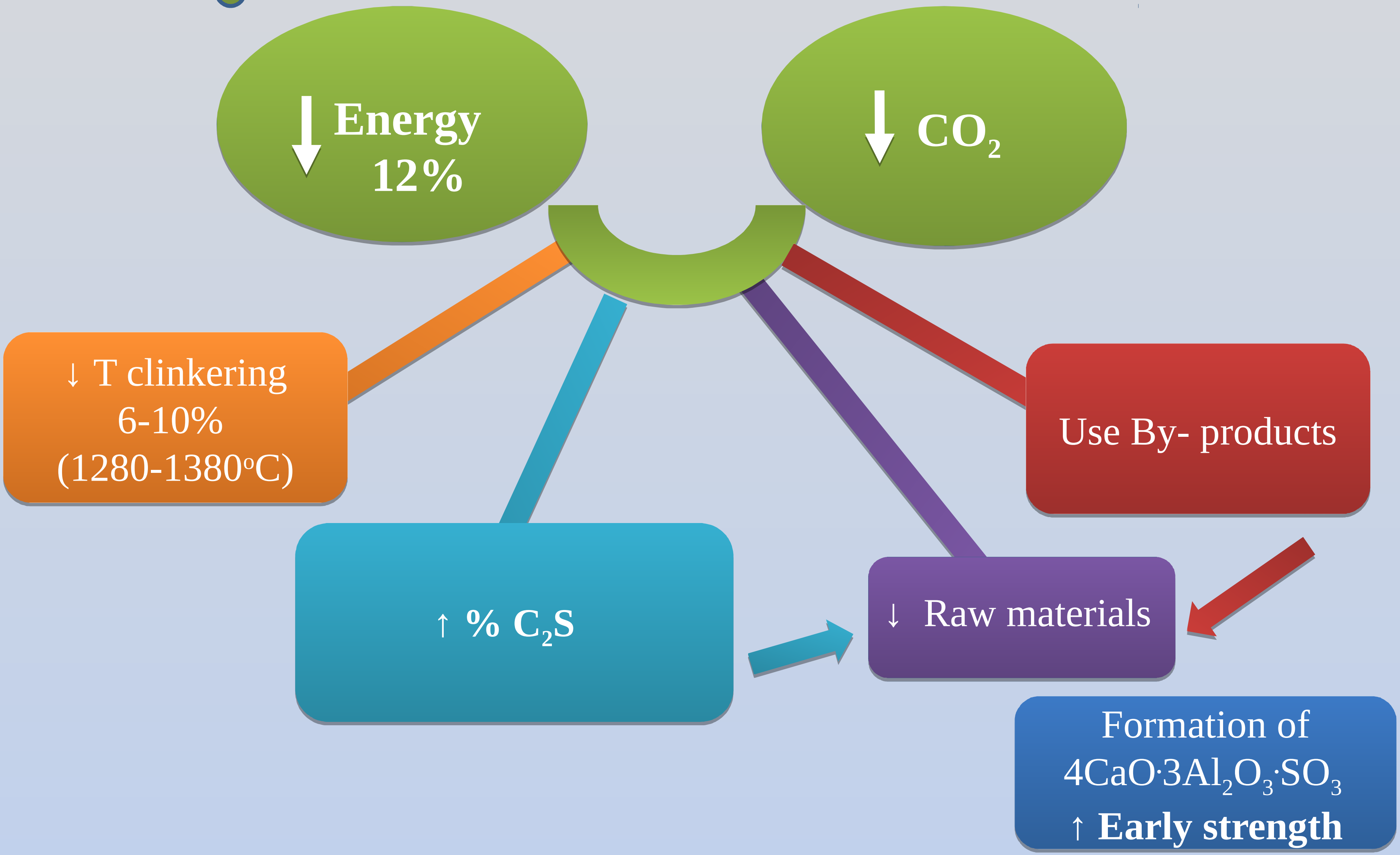
**OPC - SB**

$(CaO)_2SiO_2 < (CaO)_3SiO_2$

$1330^oC < 1450^oC$

=> ↓ **CaO** + ↓ $\mathbf{CO_2}$

# *Advantages of Sulfo-belite cements*



# *By-products*

**FGD Gypsum (Fuel Gas Desulfurization)**

(Public Power Corporation SA Hellas)

**ARR (Alumina Refined Residue)**

(Aluminium Of Greece, Mytilineos SA)

# *FGD Gypsum*

| Oxides | FGD (% wt) |
|---|---|
| $SiO_2$ | 1.52 |
| $Al_2O_3$ | 0.10 |
| $Fe_2O_3$ | 0.04 |
| CaO | **32.88** |
| MgO | 0.23 |
| $SO_3$ | **43.00** |
| LOI | 20.74 |
| Sum | 98.51 |

Uses of FGD:

- Wallboard
- Cement
- Agriculture
- other

Annual Global Production
**350 Mt** (2016)

Annual Greek Production
**10Mt**

# ARR

Annual Global Production: **119 Mt** (2016)

Annual Greek Production: **1 Mt**

| Oxides | ARR (% wt) |
|---|---|
| $SiO_2$ | 8.15 |
| $Al_2O_3$ | 17.30 |
| $Fe_2O_3$ | **38.10** |
| CaO | 11.80 |
| MgO | 0.21 |
| $SO_3$ | 0.49 |
| $Na_2O$ | 2.57 |
| $K_2O$ | - |
| $TiO_2$ | 5.76 |
| $Cr_2O_3$ | 0.29 |
| $V_2O_5$ | 0.19 |
| $P_2O_5$ | 0.14 |
| NiO | 0.097 |
| LOI | 7.00 |
| Sum | 92.00 |

# *Sulfo-Belite cement production*

- Composition design
- Experimental procedure
- Evaluation of final product

# *XRF Results*

| | Concentration of raw materials (% wt) | | | | |
|---|---|---|---|---|---|
| **Materials Oxides** | **Limestone** | **Shale** | **FGD** | **ARR** | **$Al_2O_3$** |
| $SiO_2$ | 6.25 | **53.76** | 1.52 | 8.15 | - |
| $Al_2O_3$ | 1.23 | 14.71 | 0.10 | 17.30 | **99** |
| $Fe_2O_3$ | 0.77 | 6.72 | 0.04 | **38.10** | - |
| CaO | **50.35** | 6.47 | **32.88** | 11.80 | - |
| MgO | 0.55 | 3.35 | 0.23 | 0.21 | - |
| $SO_3$ | - | 0.24 | **43.00** | 0.49 | - |
| $Na_2O$ | 0.10 | 0.77 | - | 2.57 | - |
| $K_2O$ | 0.26 | 3.48 | - | - | - |
| $TiO_2$ | - | - | - | 5.76 | - |
| $Cr_2O_3$ | - | - | - | 0.29 | - |
| $V_2O_5$ | - | - | - | 0.19 | - |
| $P_2O_5$ | - | - | - | 0.14 | - |
| NiO | - | - | - | 0.097 | - |
| **LOI** | 41.00 | 9.00 | 20.74 | 7.00 | 1.27 |
| **Sum** | 100.50 | 98.51 | 98.51 | 92.00 | 100.27 |

# Composition Design

| Experiment (%) Raw Material | $SB_{30Y}$ | $SB_{40Y}$ | $SB_{50Y}$ |
|---|---|---|---|
| **Lime** | 56.70 | 53.20 | 48.00 |
| **Shale** | 12.40 | 8.60 | 7.40 |
| **ARR** | 4.80 | 5.30 | 4.10 |
| **FGD** | 17.10 | 19.20 | 22.20 |
| **$Al_2O_3$** | 9.00 | 13.70 | 18.30 |

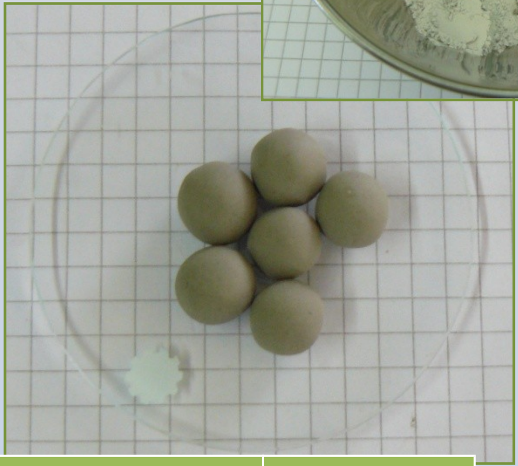
$SB_{30y}$: 30% yeelemite

$SB_{40y}$: 40% yeelemite

$SB_{50y}$: 50% yeelemite

# *Experimental Procedure*

- Raw materials supply
- Drying, Grinding, Sieving at 90μm of raw materials
- Mixing and homogenizing.
- Pelletizing (d=12 - 15mm) by adding 20-22% w/w of $H_2O$.
- Drying at 100°C for > 20h.
- Pellets fired in static kiln at 1330$^{o}$C.
- Rapid Cooling.
- Final grinding of clinker.



| T ($^{o}$C) | t (h) |
|---|---|
| 25 - 1000 | 1:00 |
| 1000 - 1000 | 0:30 |
| 1000 – 1330 | 0:40 |
| 1330 - 1330 | 0:40 |

# *Cooling of Clinker*

Air cooling and simultaneous smashing by hammer

# *Evaluation Techniques*

**Characterizatio
n
techniques**

- XRD – Q-XRD
- XRF
- Free lime determination (Javellana & Jawed, 1982)
- Specific Weight (ASTMD 854-92)
- Optical Microscopy

**Tests**

- Determination of fineness (EN 196-6)
- Compressive Strength Test (EN 197-1)

# *Results*

| Experiment / Test | $SB_{30Y}$ | $SB_{40Y}$ | $SB_{50Y}$ |
|---|---|---|---|
| F (CaO) | 0.30 | 0.67 | 1.02 |
| $W_{sp}$ (gr/cm$^3$) | 2.98 | 2.90 | 2.88 |
| Fineness (cm$^2$/g Blaine ) | 3845 | 3870 | 4100 |

# Q-XRD Results (Bogue eq.)

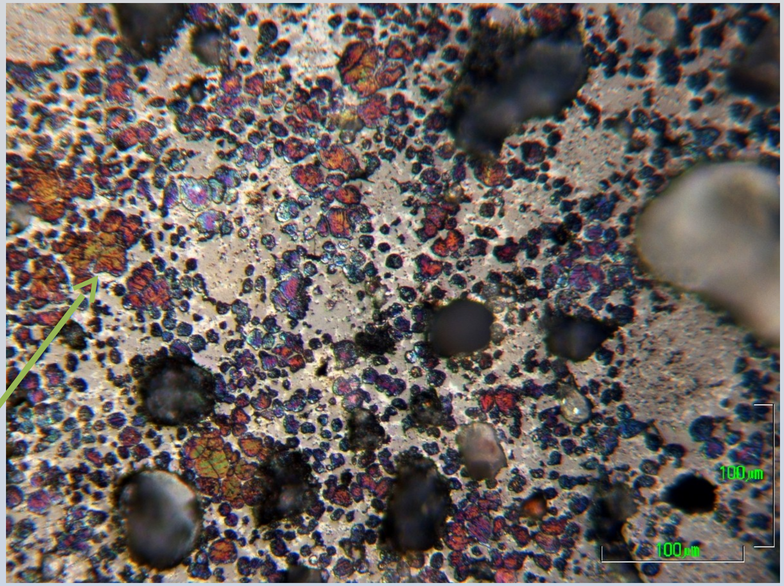
| Experiment | %$C_3S$ | %$C_2S$ | %$C_4AF$ | %$C_3A$ | %$C\hat{S}$ | %$C_4A_3\hat{S}$ |
|---|---|---|---|---|---|---|
| $SB_{30y}$ | 4.61 (-) | 39.40 (44.95) | 15.65 (14.24) | 1.77 (-) | 3.88 (11.5) | **27.01 (29.62)** |
| $SB_{40y}$ | 2.59 (-) | 28.45 (35.13) | 11.73 (13.61) | 4.32 (-) | 7.74 (10.76) | **40.44 (40.83)** |
| $SB_{50y}$ | 5.23 (-) | 21.95 (26.28) | 8.19 (10.94) | 5.12 (-) | 7.13 (10.87) | **51.96 (52.12)** |

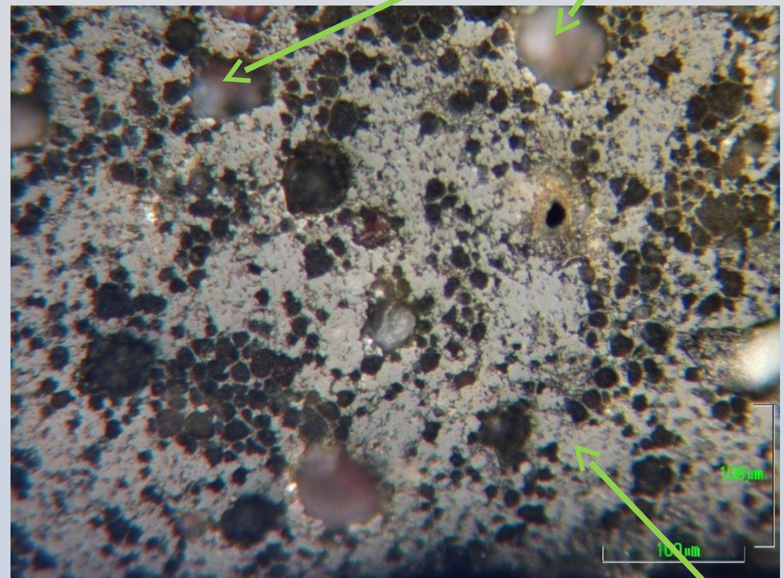
**C: CaO   S: $SiO_2$   A: $Al_2O_3$   $\hat{S}$ : $SO_3$**

# Optical microscopy

Pore & f (CaO)

***SB$_{30Y}$***



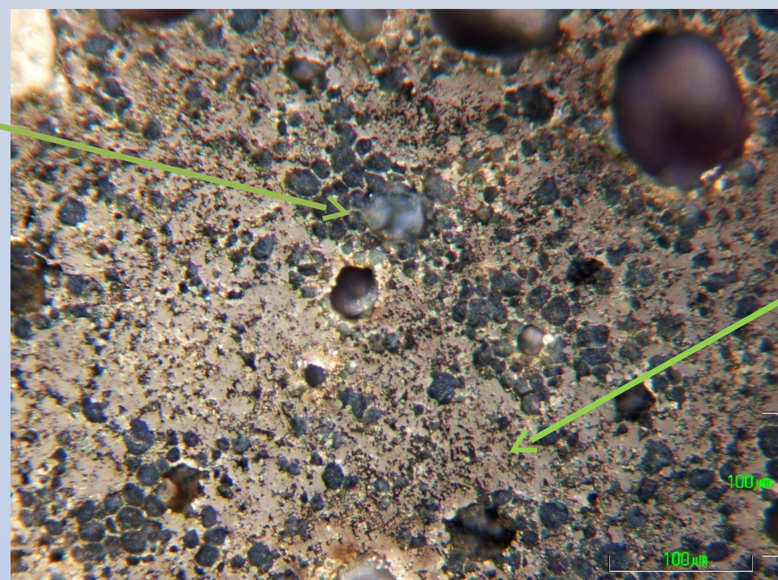




***SB$_{40Y}$***

$C_2S$

$C_4A_3\hat{S}$

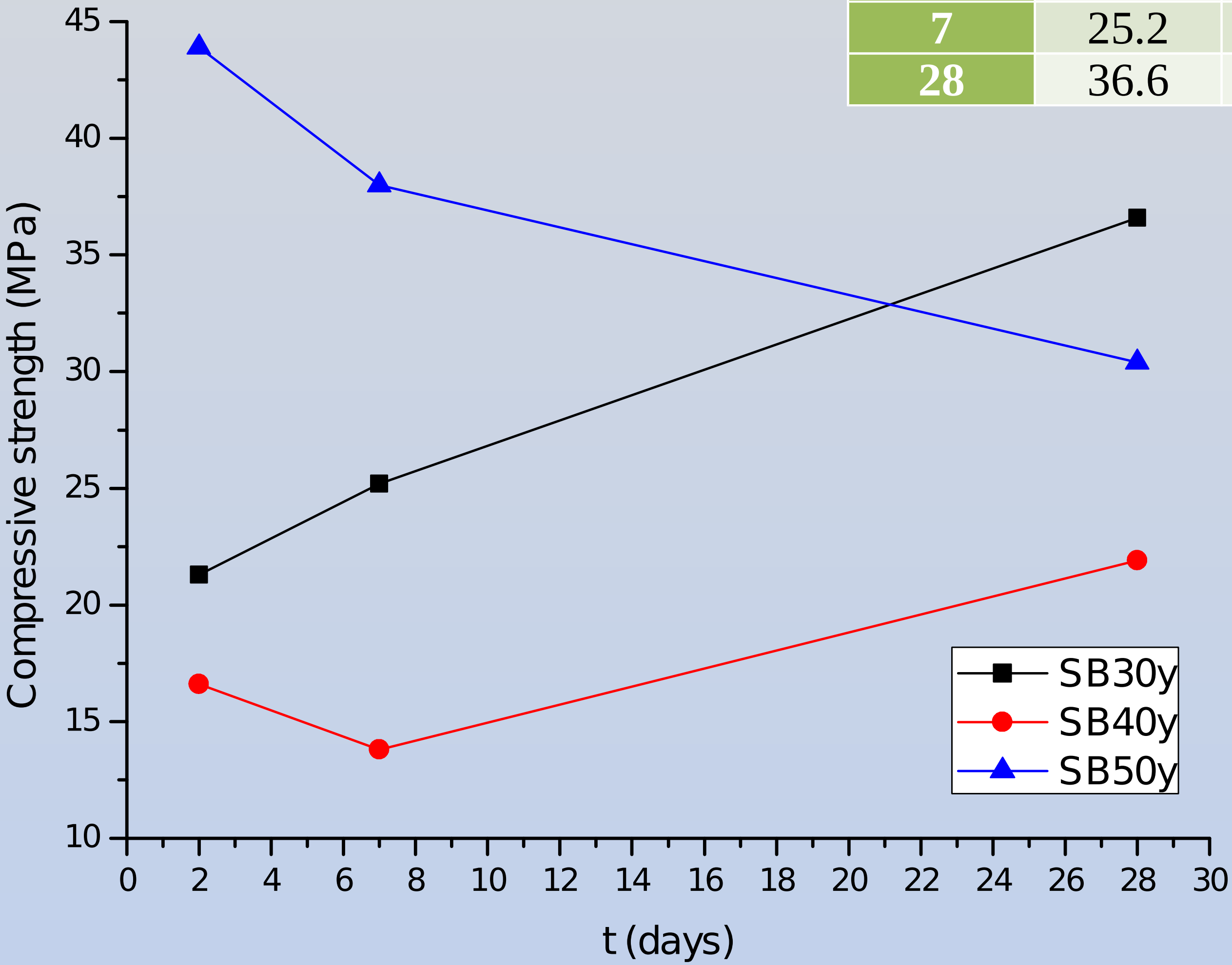
***SB$_{50Y}$***




Nital 1% etching

# *Compressive Strength*

| Exp. | $SB_{30y}$ | $SB_{40y}$ | $SB_{50y}$ | CEM 32.5N |
|---|---|---|---|---|
| (Days) | (MPa) | | | |
| 2 | 21.3 | 16.6 | 43.9 | - |
| 7 | 25.2 | 13.8 | 38.0 | >16 |
| 28 | 36.6 | 21.9 | 30.4 | 32.5-52.5 |

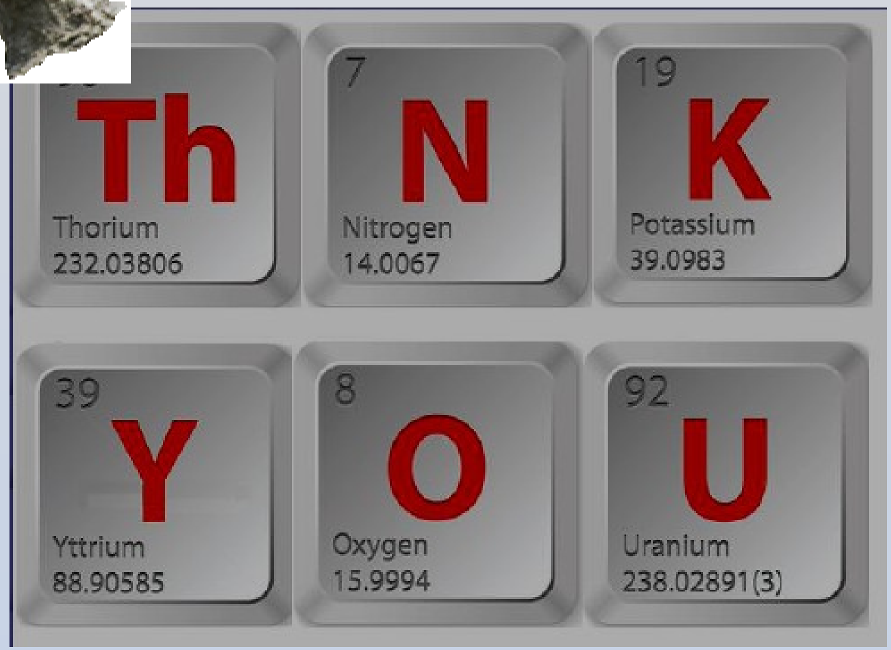


# *Conclusions*

- Industrial by-products, such as FGD and ARR, can be used as alternative raw materials to produce SBC resulting in natural resource saving.
- Production of SBC samples is achieved at lower firing temperatures, 1330C, compared to OPC, 1450$^{o}$C.
- Compressive strength values of SBC samples are within the range of the CEM 32.5N standard.
- SBC samples showed improved early strength values and later strengths comparable to OPC ones.

SB cements can be a promising alternative eco-friendly building material for special uses.

We acknowledge support of this work by:

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