

Employment of sodium aluminate waste solutions for the processing of fly-ash based geopolymers containing industrial wastes



FERNANDO CASTRO
UNIVERSITY OF MINHO
PORTUGAL

Sodium Aluminate waste solutions being tested



Generated in the process of pickling of steel matrixes from aluminum extrusion operations.

An aluminum layer is formed on the steel surface, needed to be cleaned from times to times.

The cleaning operation uses strong caustic soda solutions, to dissolve aluminum. A sodium aluminate solution + free NaOH is formed, that is discarded when reactivity is below needed.

Sodium Aluminate waste solution



pH = 13,2 – 14,2

Density = 1,20 – 1,30 g/cm³

NaAlO₂ = 60 – 90 g/l

SiO₂ (as sodium silicate) = 10 – 20 g/l

NaOH = 130 – 170 g/l

KOH = 0,2 – 0,4 g/l

SO₄²⁻ = 1 – 1,5 g/l

Industrial wastes



EAF steelmaking slag

Steelmaking ladle slag

Steel foundry slag

marble cutting and grinding sludge

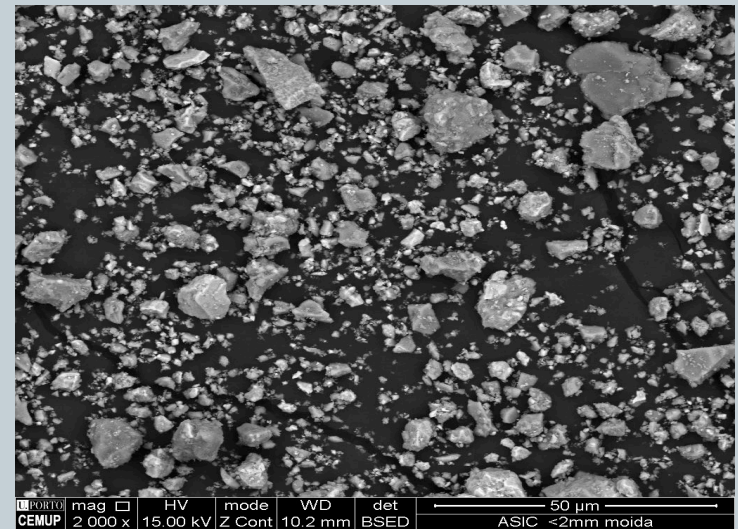
EAF Slag

Composition

Fe - 22 %
Ca - 20 %
Si - 10 %
Al - 4 %
Mg - 3 %
Mn - 3 %
Cr - 1,5 %

Rest - oxygen, nitrogen, carbon, ...

Ground to less than 2 mm



Steelmaking Ladle Slag

Composition



Ca - 46 %

Si - 8,5

S - 3,2 %

Mg - 2,8 %

Al - 1,7 %

Fe - 1,1 %

F - 0,5 %

Rest - oxygen, nitrogen, carbon, ...

Steel Foundry Slag

Composition



Si - 26 %

Mn - 15 %

Al - 6 %

Fe - 4 %

K - 3 %

Ca - 1 %

Rest - oxygen, nitrogen, carbon, ...

Ground to less than 2 mm

Marble cutting and grinding sludge

Composition



97 % CaCO_3 in dry basis. Some Mg and Si

Employed as it is, after drying. Particles from 1 to 20 μm

Testing



Based on system Fly Ash + sodium aluminate solution + wastes + feldspatic sand

Sand was replaced partially or totally by EAF and foundry slags

Mixing for 15 minutes, resting for 6 hours and then curing at 80 °C, 24 hours

Making 16 x 4 x 4 cm samples

Flexural and compression strength measured at 7 and 28 days (3 samples each)

Incorporation of different amounts of wastes, to test effect on compression and flexural strength

Testing



Employed materials

Class F Fly Ash composition

SiO₂	- 52,3 %
Al₂O₃	- 21,9 %
Fe₂O₃	- 11,5 %
K₂O	- 2,8 %
CaO	- 2,1 %
MgO	- 1,9 %
Na₂O	- 1,7 %
TiO₂	- 1,5 %
C	- 1,9 %

Testing

Fly ash

(SEM, BSED)

Identified phases:

Z1 - Fe - Ca - Mg oxide + some S

Z2 - Fe_2O_3

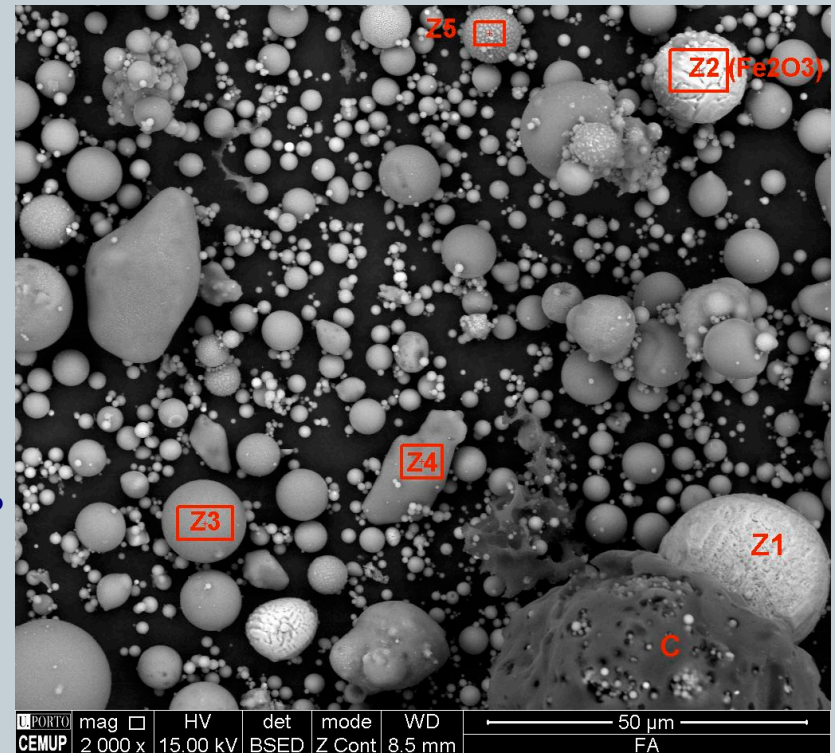
Round “glassy” particles (Z3)

SiO_2 - 57%; Al_2O_3 - 30%; MgO - 3,4%; Na_2O - 2,0

Z4 - SiO_2

Round “glassy” particles (Z5)

SiO_2 - 40%; Al_2O_3 - 28%; Fe_2O_3 - 20%; MgO - 9%



Testing



A total of 50 different mixtures

Fly ash – from 13 to 36 %

Aluminate waste solution – from 10,5 to 20 %

Sand – from 0 to 70 %

Ladle slag – from 0 to 7 %

Marble sludge – from 0 to 10 %

EAF slag – from 0 to 60 %

Foundry slag – from 0 to 60 %

Testing



Results



CR_{7 days} from 4 to 36 MPa
FR_{7 days} from 1,5 to 6,8 MPa

CR_{28 days} from 6 to 37 MPa
FR_{28 days} from 1,7 to 8,7 MPa

Multivariate analysis of CR and FR (MPa) in terms of composition of mixtures, in weight %

Sand, EAF slag and Foundry slag have no significant effect on CR and FR, both for 7 and 28 days. Ladle Slag (LS) has significant effect on CR at 7 days.

Fly ash (FA) and marble sludge (MS) increase CR and FR, weather sodium aluminate solution (NaAl) decreases them.

Results



$$\mathbf{CR_7 = 34,2 + 0,59 \times FA - 2,3 \times NaAl + 0,61 \times LS + 0,90 \times MS}$$

with $r^2 = 0,74$

$$\mathbf{CR_{28} = 31,2 + 0,82 \times FA - 2,3 \times NaAl + 1,19 \times MS}$$

with $r^2 = 0,73$

Results



$$\mathbf{FR_7 = 4,48 + 0,17 \times FA - 0,38 \times NaAl + 0,35 \times MS}$$

with $r^2 = 0,64$

$$\mathbf{FR_{28} = 6,02 + 0,18 \times FA - 0,47 \times NaAl + 0,49 \times MS}$$

with $r^2 = 0,57$

Results



Some good results

60 % Foundry slag + 20 % FA + 12 % NaAl + 8 % MS

CR₂₈ = 37 MPa FR₂₈ = 8,2 MPa

51 % EAF slag + 35 % FA + 14 % NaAl

CR₂₈ = 29 MPa FR₂₈ = 7,6 MPa

Results



Some less good results

58 % sand + 14 % FA + 18 % NaAl + 10 % MS

CR₂₈ = 7 MPa FR₂₈ = 2,6 MPa

30 % sand + 24 % foundry slag + 16 % FA + 20 % NaAl + 10 % MS

CR₂₈ = 6 MPa FR₂₈ = 3,8 MPa

Conclusions



Sodium aluminate waste solution is able to produce geopolymers together with other industrial wastes

Amount of solution has to be limited to around 10 – 12 %

Replacement of sand by foundry, EAF and ladle slags has no significant effect

Fly ash and marble sludge increase both compression and flexural strength