CYPRUS 2016 4th International Conference
on Sustainable Solid Waste Management

23nd - 25th June 2016
Limassol, Cyprus

Valorisation of Woody Biomass Bottom Ash in Portland Cement: A Characterization and Hydration Study

V. Sklivaniti [1], P.E. Tsakiridis [2], N.S. Katsiotis [1], D. Velissariou [1], N. Pistofidis[3], D. *Papageorgiou*[3]
M. Beazi [1]

[1] Laboratory of Inorganic & Analytical Chemistry, *School of Chemical Engineering, N.T.U.A.*
[2] Laboratory of Physical Metallurgy, *School of Mining and Metallurgical Engineering, N.T.U.A.*
[3] Titan Cement Company SA, Group R&D and Quality Department, Athens, Greece

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Environmental Concerns

- **Research for Alternative renewable energy resources/ Alternative Raw Materials**
  - Benefit of the economical cost
  - Reduction of the environmental impact
- **Energy Substitutes could lead to a relative increase of wasted produced, during the incineration process**
  - Bottom ash
  - Fly ash

Bottom/Fly Ash Production

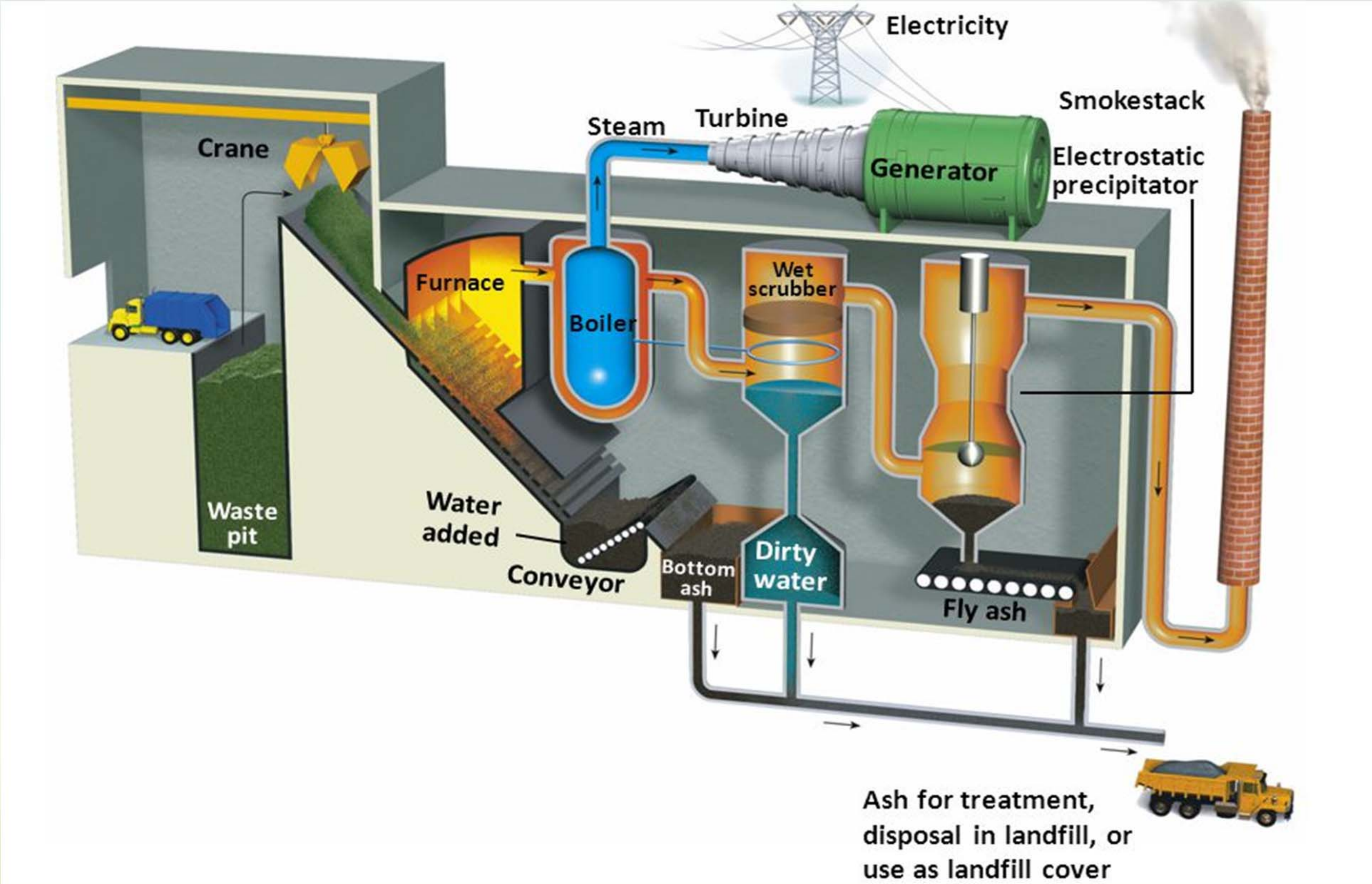
Bottom ash

- produced in the boiler first combustion chamber
- main part of the ash generated,
- mixed with other impurities

Fly ash

- collected primarily in cyclones, which are located behind the combustion unit
- and in electrostatic and/or bag filters
- may be rich in heavy metal contaminants

Waste to Energy Incinarator



Valorization of Ash

- From biomass for energy production
- Material chemical constituents can vary considerably but all ashes include:
  - Silicon Dioxide (SiO2)
  - Calcium Oxide (CaO) also known as Lime
  - Iron (III) Oxide (FeO2)
  - Aluminum Oxide (Al2O3)
- Environmental regulations in Europe obligate to the choice of recycling and reuse
- Disposal cost is very high at controlled landfills
- Utilization Pathways as
  - raw material in ceramic industry
  - filler material in road bases construction
  - neutralize agent for wastes with high acidity,
  - glazing Material
  - filler material in concrete
  - substitute in cement, mainly because of its high alkali content

Portland cement

"Cement is a crystalline compound of calcium silicates and other calcium compounds having hydraulic properties"

- Hydraulic ability: to set and harden under or with excess water through the hydration of the cement's chemical compounds or minerals
- There are two Reaction Mechanisms:
  - Activation with the addition of water (Hydration Reaction)
  - Development of hydraulic properties when the interact with hydrated lime $Ca(OH)_2$ (Pozzolanic Reaction)
- Waste derived or by-product materials can be utilised from cement industries in multiple ways:
  - to replace primary raw materials used in the cement clinker recipe •
  - to substitute conventional fuels such as coal, coke, and gas.
  - to be utilised as additives in the production process of constituent cements to meet the requirements of EN 197-1

Materials & Methods

- The cement used in all mixtures was a CEM I 52.5 Ordinary Portland Cement (OPC)
- The bottom ash had been generated after the combustion of olive plants trimmings in wood-fired boilers

Table 1.Composition and characteristics of cement mixtures

Code	CEM I 52.5N (wt%)	WBA (wt%)	Specific Surface Area (cm^2/g)	Specific Gravity (g/cm^3)
C_{Ref}	100	0	3870	3.14
C_2	98	2	3870	3.13
C_3	97	3	3870	3.12
C_5	95	5	3875	3.10
C_7	93	7	3875	3.08
C_{10}	90	10	3880	3.06

Materials & Methods

- **Particle size distribution**
- **Chemical analysis**
  - X-ray Fluorescence & Atomic Absorption Spectrophotometry
- **Crystalline phases of both WBA and CEM I 52.5**
  - XRD analysis
- **Semi-quantitative phases analysis**
  - Rietveld Algorithm
- **The morphology of WBA**
  - Scanning Electron Microscopy (SEM) & Transmission electron microscopy
- **Hydration Study**
  - XRD analysis & TG/DTA

Results-Woody Bottom Ash Characterization- WBA particle size distribution & Particle size distribution mean values specific surface area results

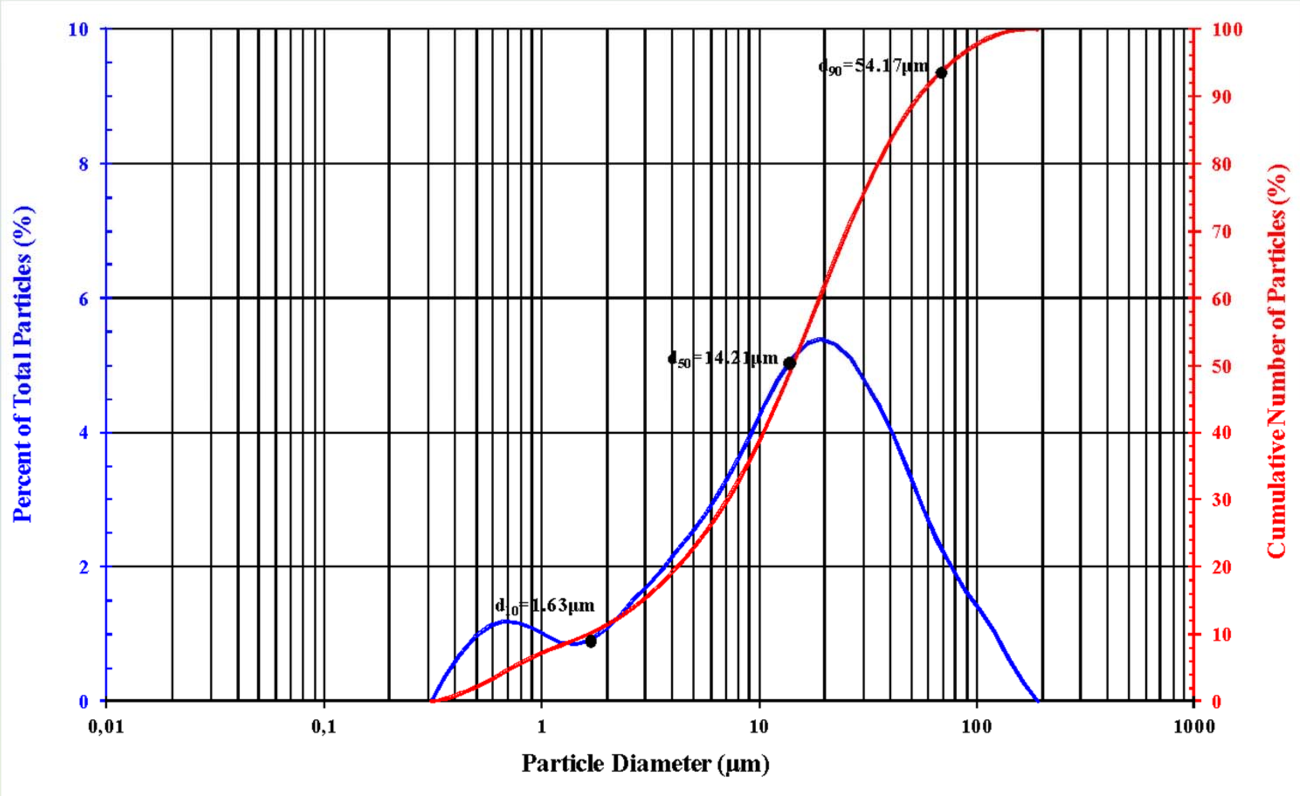


Figure 1: WBA particle size distribution (Cumulative Passing and Particle Distribution)

Table 2 Particle size distribution mean values

Sample	PSD			
	Mean (µm)	Median (µm)	x_{10} (µm)	x_{90} (µm)
WBA	1.15	14.21	1.63	54.17

Results-Woody Bottom Ash Characterization-
Chemical analysis

Table 3 Chemical analysis and physical characteristics of cement and ash used

Oxides	Chemical Analysis (wt%)	
	CEM I 52.5N	WBA
SiO_2	21.25	6.84
Al_2O_3	3.77	2.73
Fe_2O_3	4.27	1.39
CaO	64.35	**31.41**
MgO	1.25	2.45
K_2O	0.44	**12.31**
Na_2O	0.12	0.11
SO_3	2.40	0.14
TiO_2	0.23	
free CaO	0.15	1.60
Cl	0.018	0.05
LOI	1.25	41.49
Physical Characteristics		
Specific surface (cm^2/g)	3870	3930
Specific gravity (g/cm^3)	3.14	2.35

Results-Woody Bottom Ash Characterization-
Chemical analysis and physical characteristics of cement and ash used

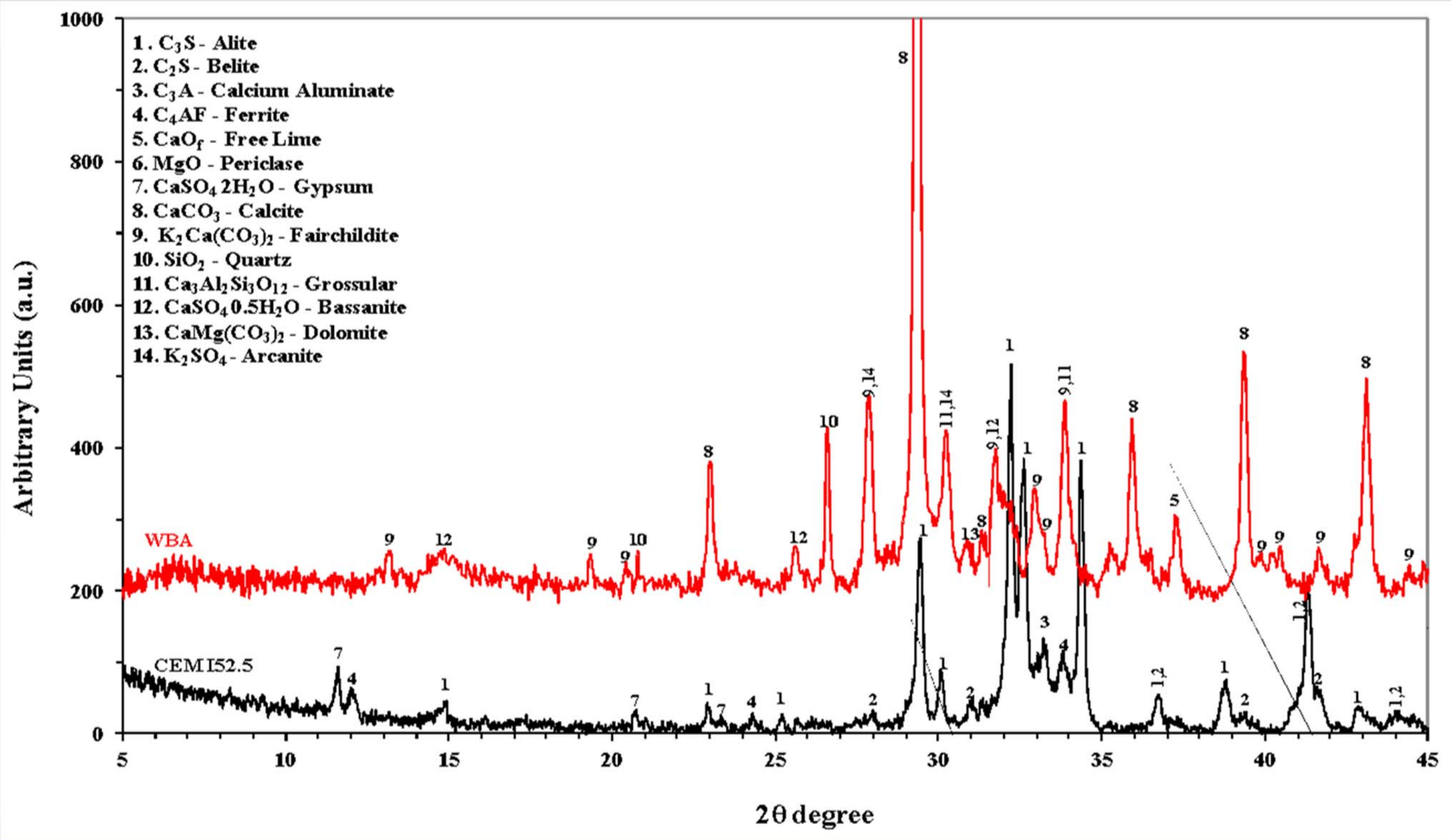


Figure 2: X-ray diffraction analysis of cement and ash used

Results-Woody Bottom Ash Characterization-
WBA phase composition by Rietveld analysis

Table 2. WBA phase composition by Rietveld analysis

Phases	Composition (wt%)
	WBA
$CaCO_3$ - Calcite	67.6
K_2CaCO_3 - Fairchildite	8.7
SiO_2 –Quartz	7.8
$Ca_3Al_2Si_3O_{12}$ - Grossular	6.5
K_2SO_4 - Arcanite	4.1
$CaSO_4$ $0.5H_2O$ - Bassanite	2.5
CaO - Lime	1.6
$CaMg(CO_3)_2$ - Dolomite	1.2

Woody Bottom Ash Characterization- Scanning electron micrographs of WBA.

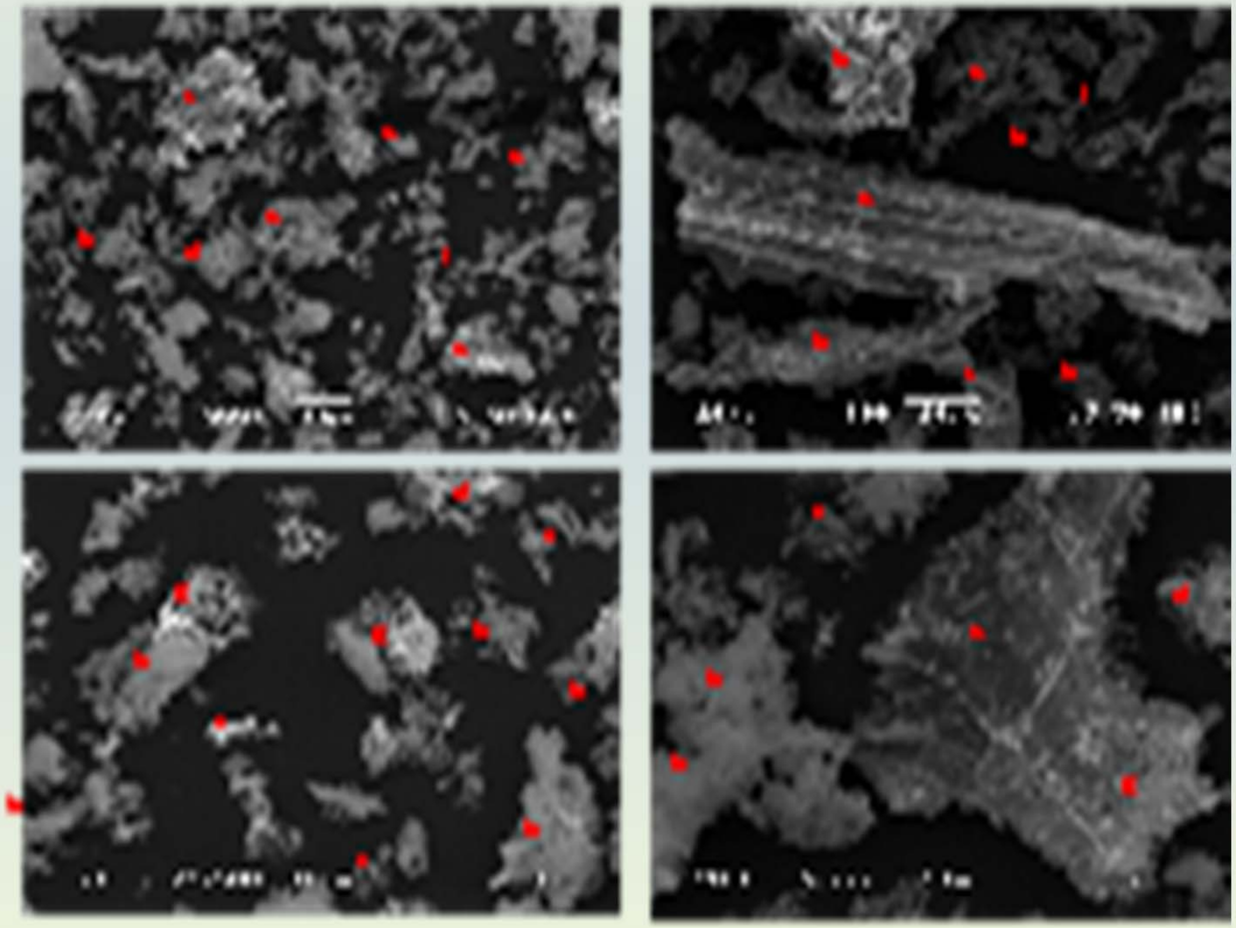


Figure 3: Scanning electron micrographs of WBA. a: $CaCO_3$, b: K_2CaCO_3, c: SiO_2, d: $Ca_3Al_2Si_3O_{12}$ e:K_2SO_4, f: $CaSO_4$ $0.5H_2O$, g:CaO

Results-Woody Bottom Ash Characterization-Transmission electron microscopy

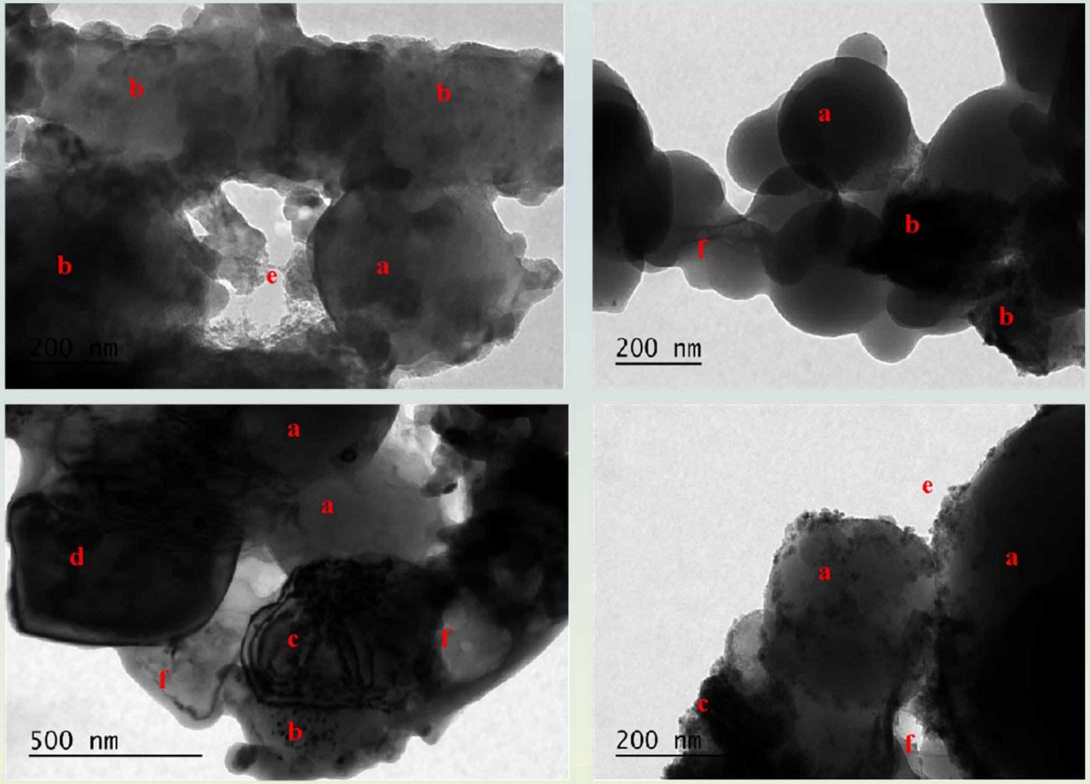


Figure 4: Transmission electron microscopy of WBA . a: $CaCO_3$, b: K_2CaCO_3, c: SiO_2, d: $a_3Al_2Si_3O_{12}$ e: K_2SO_4, f: CaO

Results-Blended Cements

Table 4. Physical properties of blended cements

Sample	WBA (wt%)	Water Demand (wt%)	Setting Times (min)		Le Chatelier Expansion (mm)
			Initial	Final	
C_{Ref}	-	26.60	120	165	0.5
C_2	2	27.40	175	250	0.6
C_3	3	28.20	70	225	0.7
C_5	5	29.20	50	170	0.9
C_7	7	31.75	<40	150	1.2
C_{10}	10	32.40	<40	120	1.7

Results-Blended Cements - Strength development

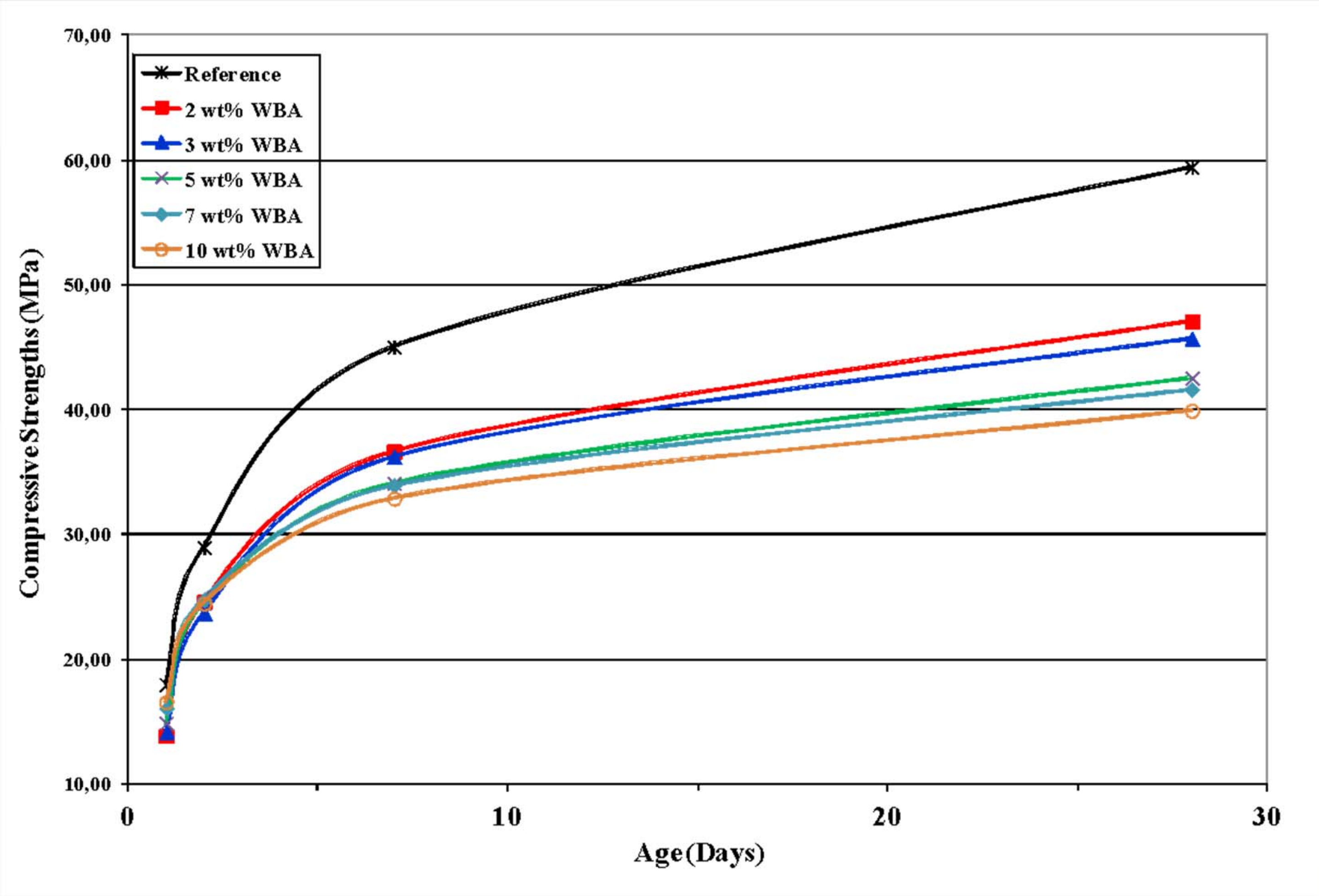


Figure 5: Strength development of the produced blended cement with WBA

Results-Blended Cement Hydration - 7wt% WBA substitution

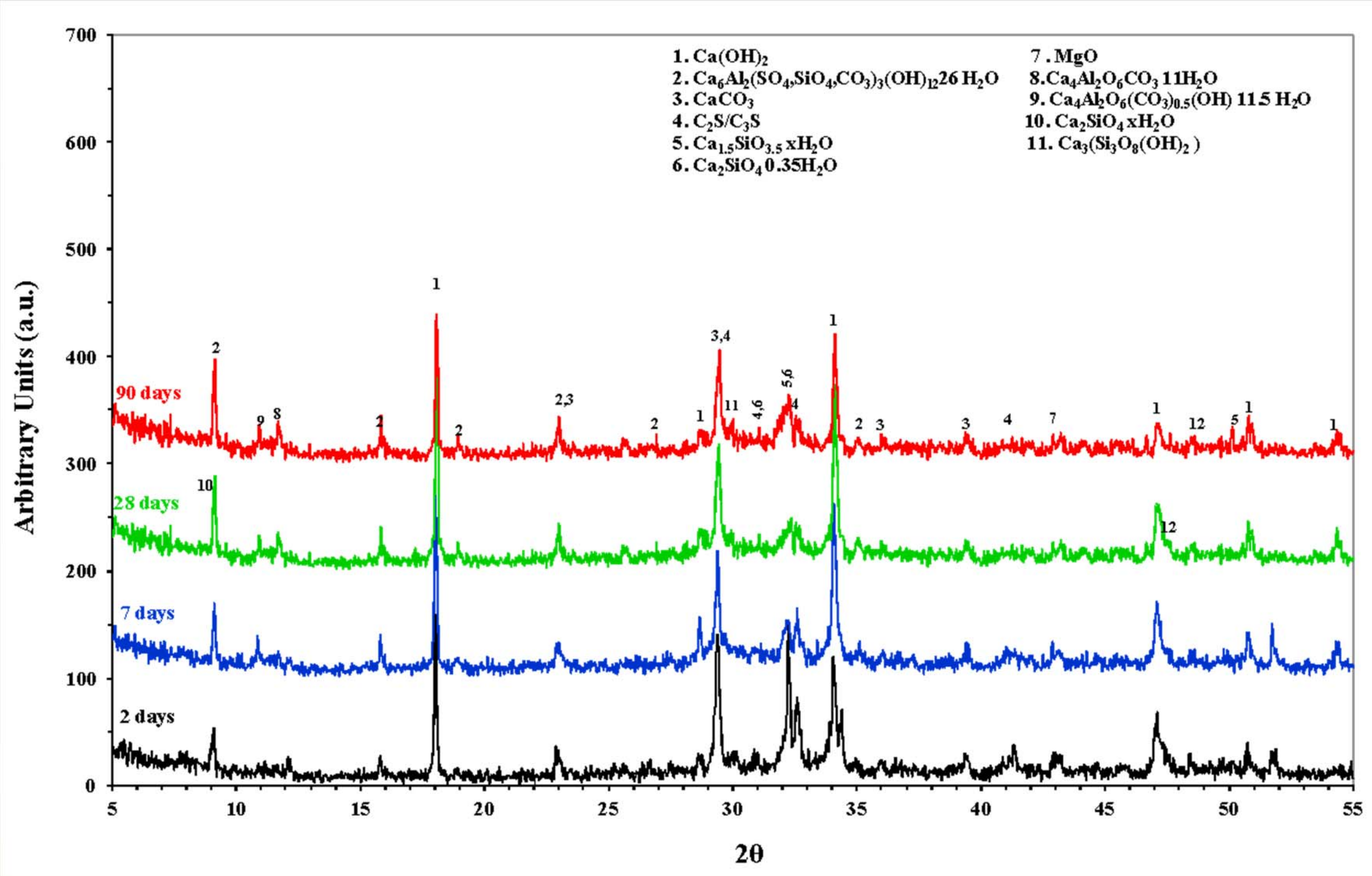


Figure 5: X-ray diffraction of C_7 blended cement with 7 wt% WBA, hydrated at various ages

Results-Blended Cement Hydration - hydrated at 28 days

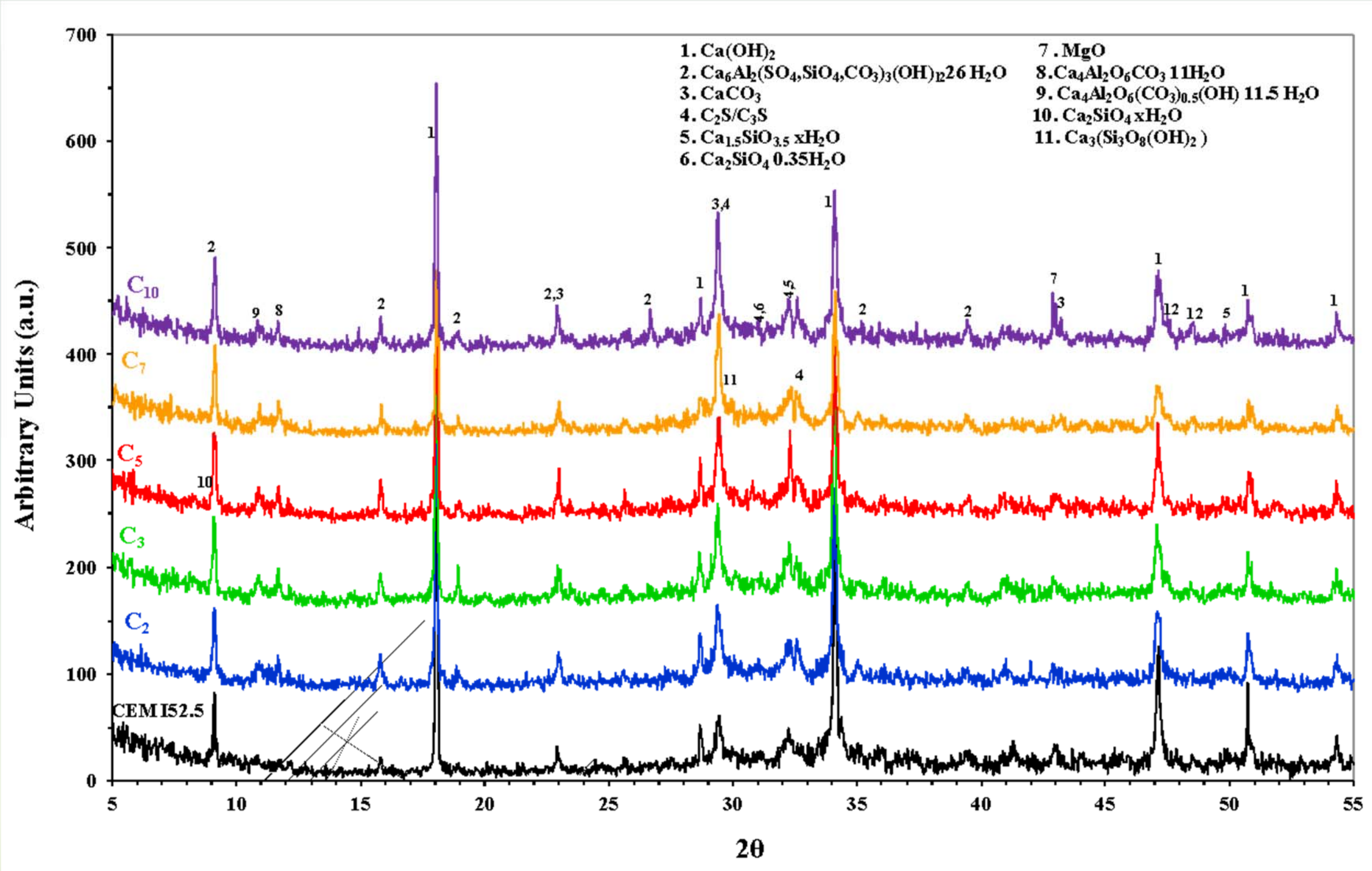


Figure 6: X-ray diffraction of reference and blended cements, hydrated at 28 days

Results-Blended Cement Hydration - hydrated at 28 days

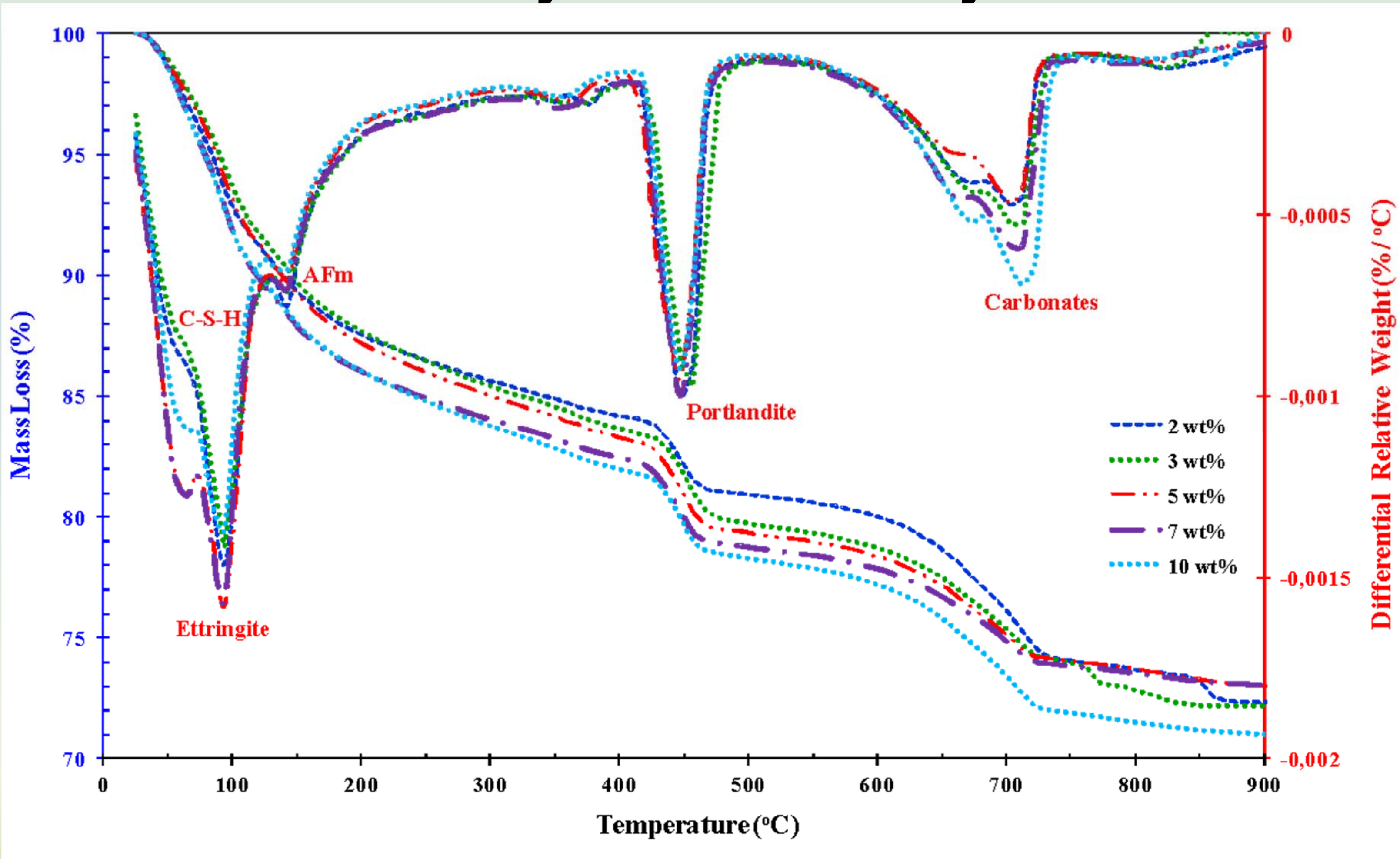


Figure 7: TG/DTG of blended cements, hydrated at 28 days

Conclusions

-- Woody bottom ash (WBA) is:

-combustion by-product of olive plants trimmings in wood-fired boilers, is

-carbonate fine grained material, consisting mainly of calcite ($CaCO_3$) and secondarily of fairchildite (K_2CaCO_3)

--Substituting Portland cement can be used as a filler material,

-shorter setting times

-higher water demand

-hydration rate acceleration.

-relatively lower compressive strengths at all ages

--Up to 7 wt% substitution can be satisfied the requirements for strength class 42.5 as per EN 197-1