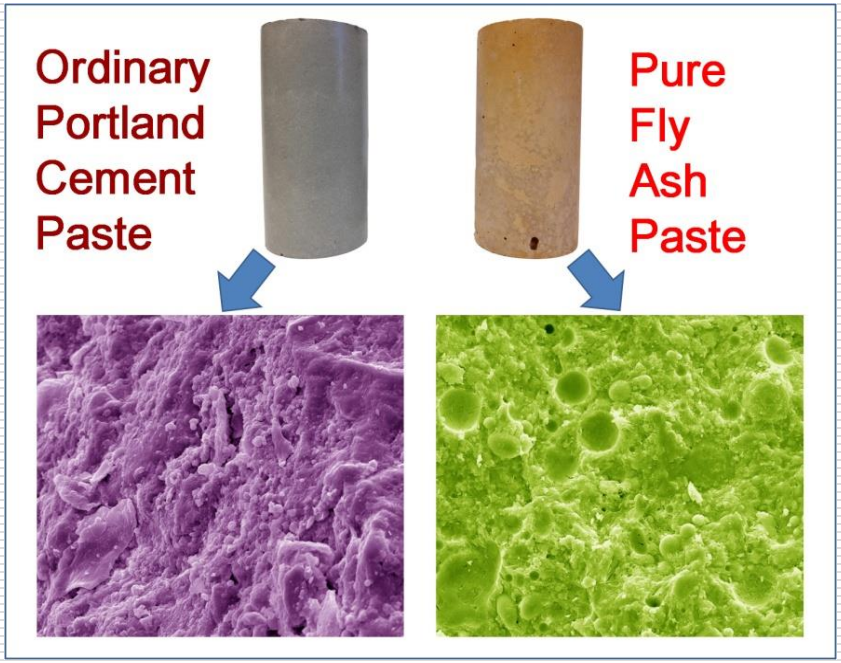
# Development of durable "green" concrete exposed to deicing chemicals via synergistic use of locally available recycled materials and multi-scale modifiers

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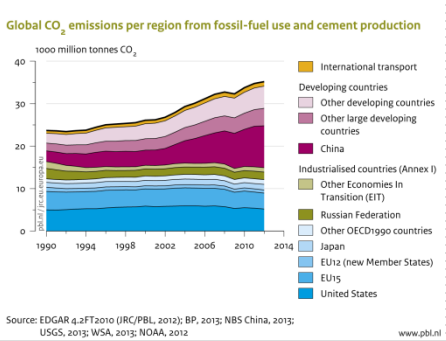
# Background

## 1. Extensive energy consumption of cement production

- Cement production: over 5 billion tons per year
- 1 ton $CO_2$/1 ton cement




✓ 150 million tons of high quality coal/year

✓ Contribute 7-8% $CO_2$ emission

✓ Limitation of natural resources

**It is necessary to use up-cycling waste materials as Green binders to mitigate the environmental problems**

# Background

- ✓ Coal fly ashes (CFA) are the main by-products of coal combustion for electrical energy production. They are considered as a type of solid waste with high levels of contaminants, and thus pose a substantial environmental.
- ✓ The U.S. generates approximately 70 million tons of CFAs, of which only 27 percent (~19 million tons) are recycled and the rest are landfilled.

# Project Scope

- Objective

*The main objective of this project* is to develop a new technology by synergistically using multi-scale modifiers and local low-cost or recycled materials to prepare "green" cementitious binder.

# Materials and mix design

1. CFA: Corette electric power plant in Billings, MT, USA

2. OPC: C150-07 Type I/II low-alkali Portland cement (ASH Grove Cement Company, Clancy, MT

**The mix design of the pure fly ash paste and the ordinary Portland cement paste**

| Mix design parameter | Ordinary Portland Cement paste | Pure Fly Ash paste |
|---|---|---|
| Water/binder ratio | 0.40 | 0.20 |
| Borax (wt.% of fly ash) | - | 0.20 |
| Fly ash content | - | 100% |
| Cement content | 100% | - |

# Chemical composition of the fly ash and cement (wt.%)

| Component | Coal Fly Ash | Cement |
|---|---|---|
| $SiO_2$ | 29.5 | 20.4 |
| $Al_2O_3$ | 17.3 | 3.7 |
| $Fe_2O_3$ | 6.5 | 3.4 |
| $SO_3$ | 3.5 | 2.6 |
| CaO | 30.6 | 63.3 |
| $P_2O_5$ | 1.3 | - |
| $Na_2O$ | 3.1 | 0.1 |
| $K_2O$ | 0.4 | 0.4 |
| MgO | 5.3 | 3.2 |
| $TiO_2$ | 1.6 | - |

# Materials preparation

For PFAP sample preparation, the borax was dissolved in the water before the water was mixed with the fly ash.

After mixing, the fresh paste was cast into polyvinyl chloride (PVC) molds to form $\Phi$ 50.8 mm (diameter) $\times$ 101.6 mm (length) cylinders, and was carefully compacted to minimize the amount of entrapped air.

The paste specimens were de-molded after 24 h at room temperature, and then cured in a wet chamber (20 $\pm$ 2°C, relative humidity: 95%) for additional days.

# Properties testing

The compressive strength test followed ASTM C109 and the loading rate was 0.5 mm/min. The average measurement from 6 samples was used as the final data value.

The gas permeability test was performed using liquid methanol as the gas source to determine the gas transport properties of 28-d cured paste specimens.

The chloride anion (Cl-) permeability of water-saturated, 28-d cured paste specimens was tested via electromigration experiments on a setup featuring a disc-shaped specimen that separated the Cl- source (a solution of 3% NaCl and 1% NaOH) and the Cl- destination (a solution of 1% NaOH ).

# Microstructure characterization

The scanning electron microscopy (SEM)/Energy Dispersive Spectrometer (EDS) was performed on an FEI-Quanta 200F scanning electron microscope under an accelerating voltage of typically 20 kV.

Nano-indentation was employed to characterize the hardness and modulus of the plate specimens. It was performed following the continuous stiffness measurement (CSM) method with a Nano Indenter XP from American MTS Corporation.

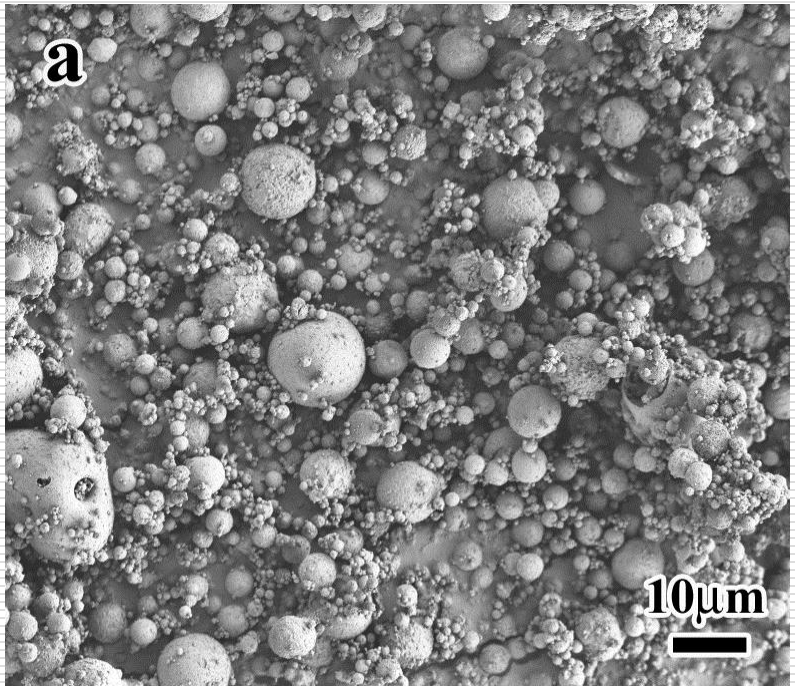
The thermal properties of the paste powder samples were characterized by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA), using a Mettler Toledo-TGA/SDTA851$^{e}$.

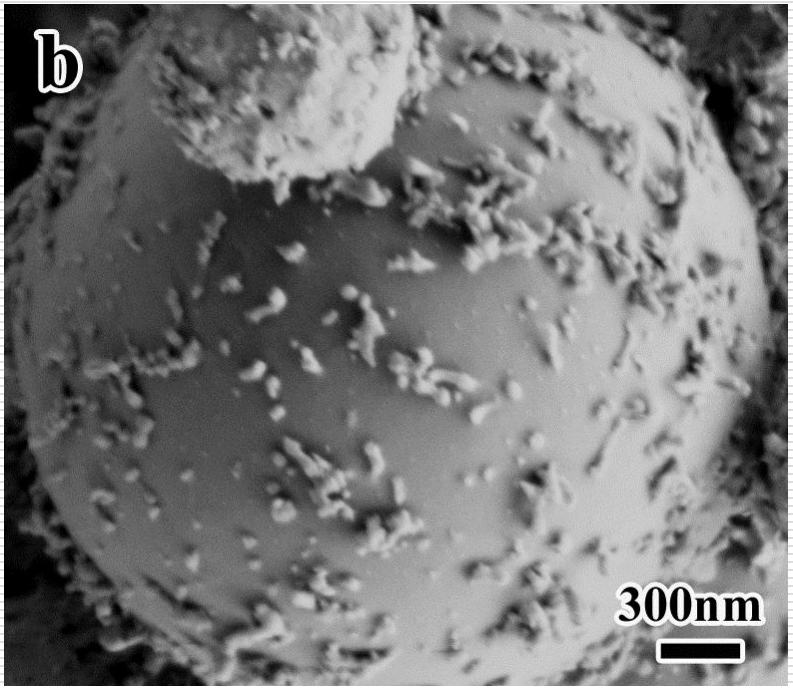
X-ray diffraction (XRD) patterns of the paste specimens were obtained on a Rigaku D/max-rA X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å).

# Properties of the PFA paste and OPC paste

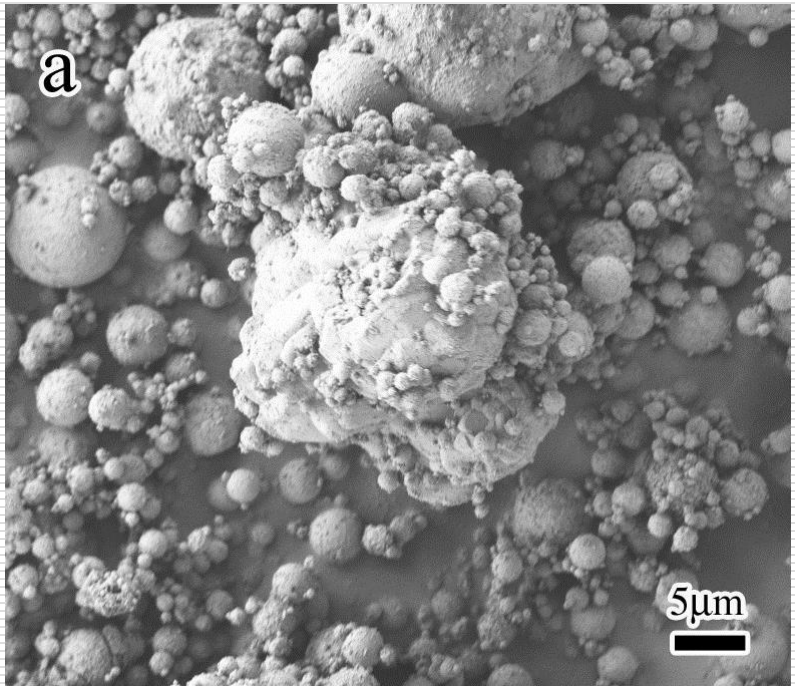
| Properties | ordinary Portland cement paste | pure fly ash paste |
|---|---|---|
| Slump (mm) | 216 | 121 |
| 28-d Compressive strength (MPa) | 56 | 36 |
| Bulk Dry Density (g/cm$^3$) | 2.0 | 1.6 |
| Surface Resistivity (kΩ·cm) | 6.2 | $1.3 \times 10^2$ |
| Bulk Resistivity (kΩ·cm) | 12 | $1.5 \times 10^4$ |
| Hardness, H (GPa) | 1.4 | 1.8 |
| Elastic Modulus (GPa) | 37.6 | 39.4 |
| Gas permeability coefficient, k ($10^{-17}$ m$^2$/s) | 4.8 | 4.1 |
| Chloride diffusion coefficient, D ($10^{-12}$ m$^2$/s) | 1.5 | 1.9 |
| Q (mS/cm$^2$) | 217 | 147 |
| R (kΩ.cm$^2$) | 35 | 154 |

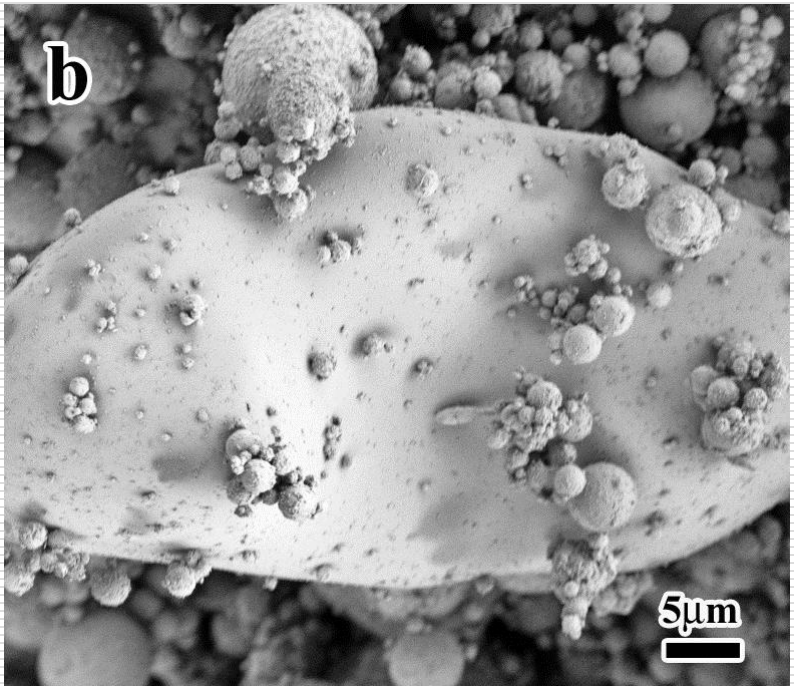
# Low and high magnification SEM micrographs of the CFA spheres



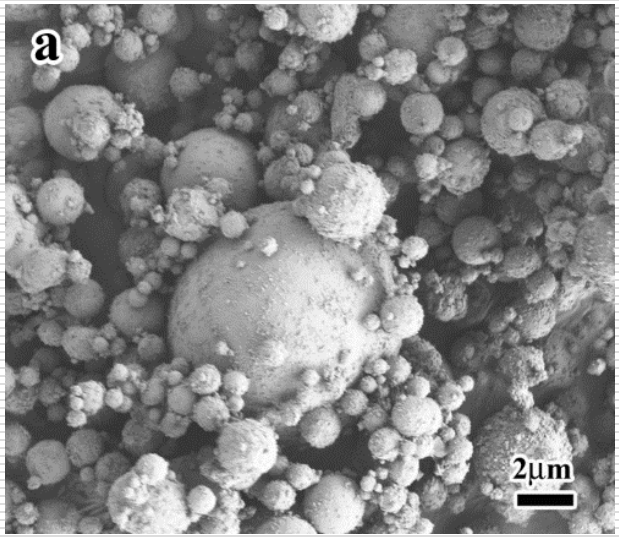



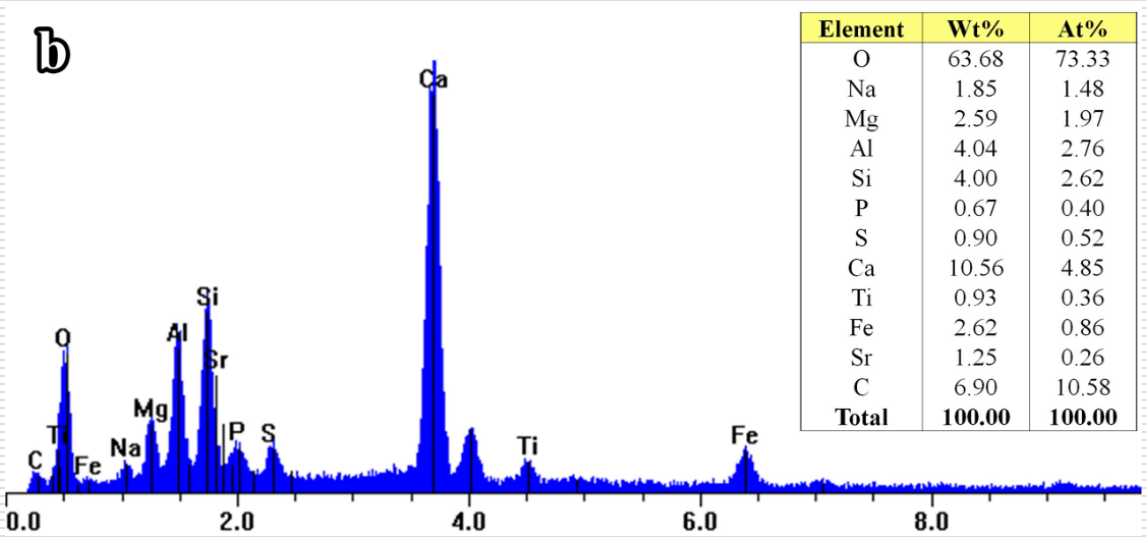
# SEM morphologies of the non-spherical fly ash particles



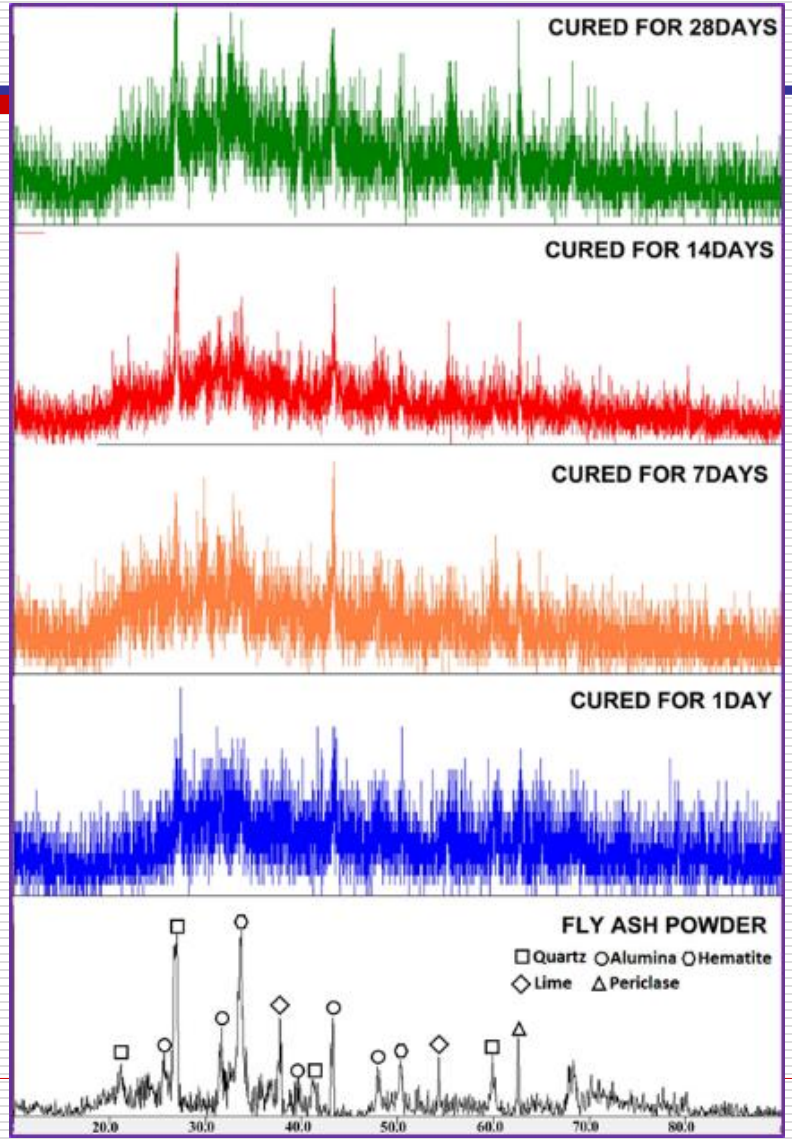
# SEM/EDS analysis of the fly ash particles



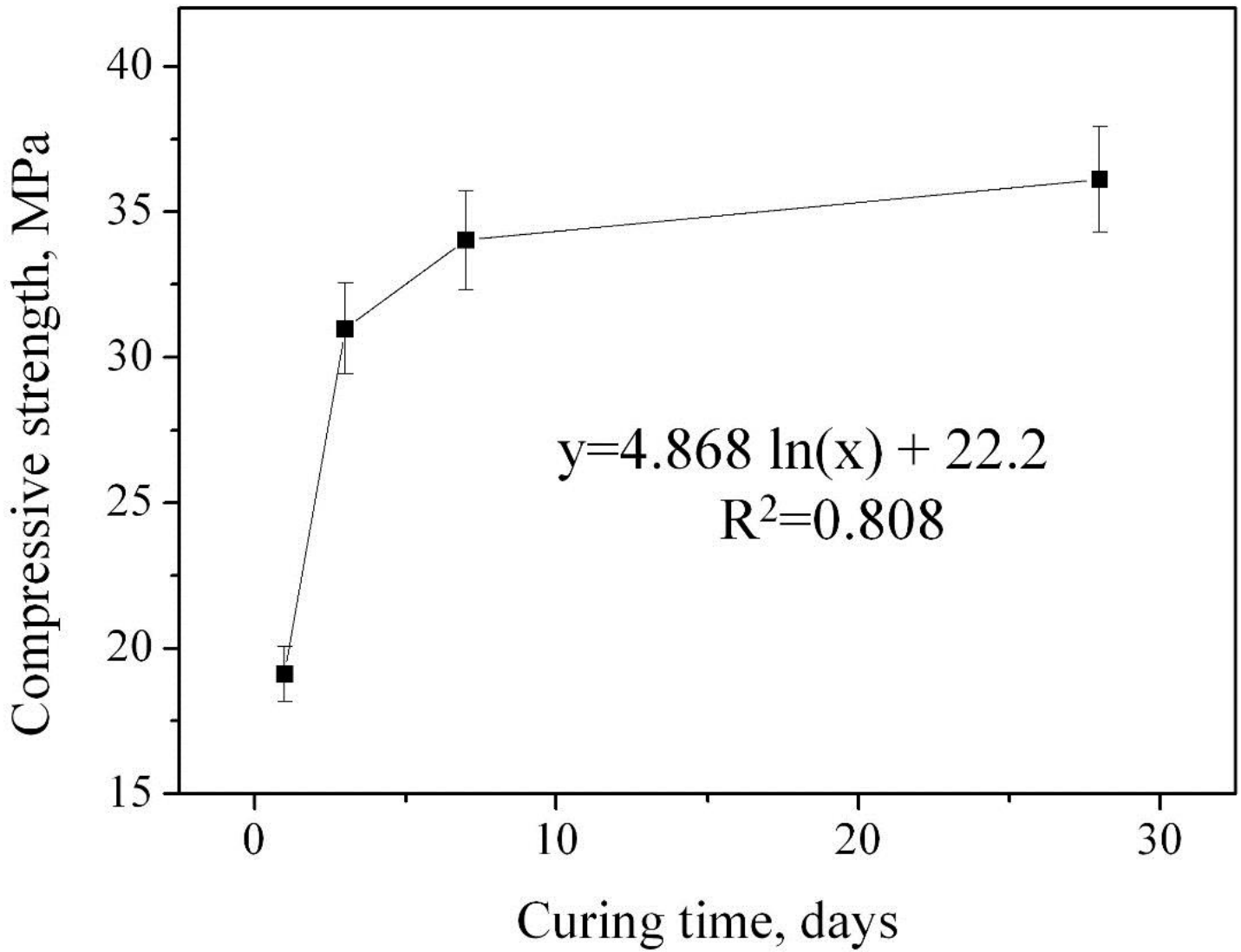



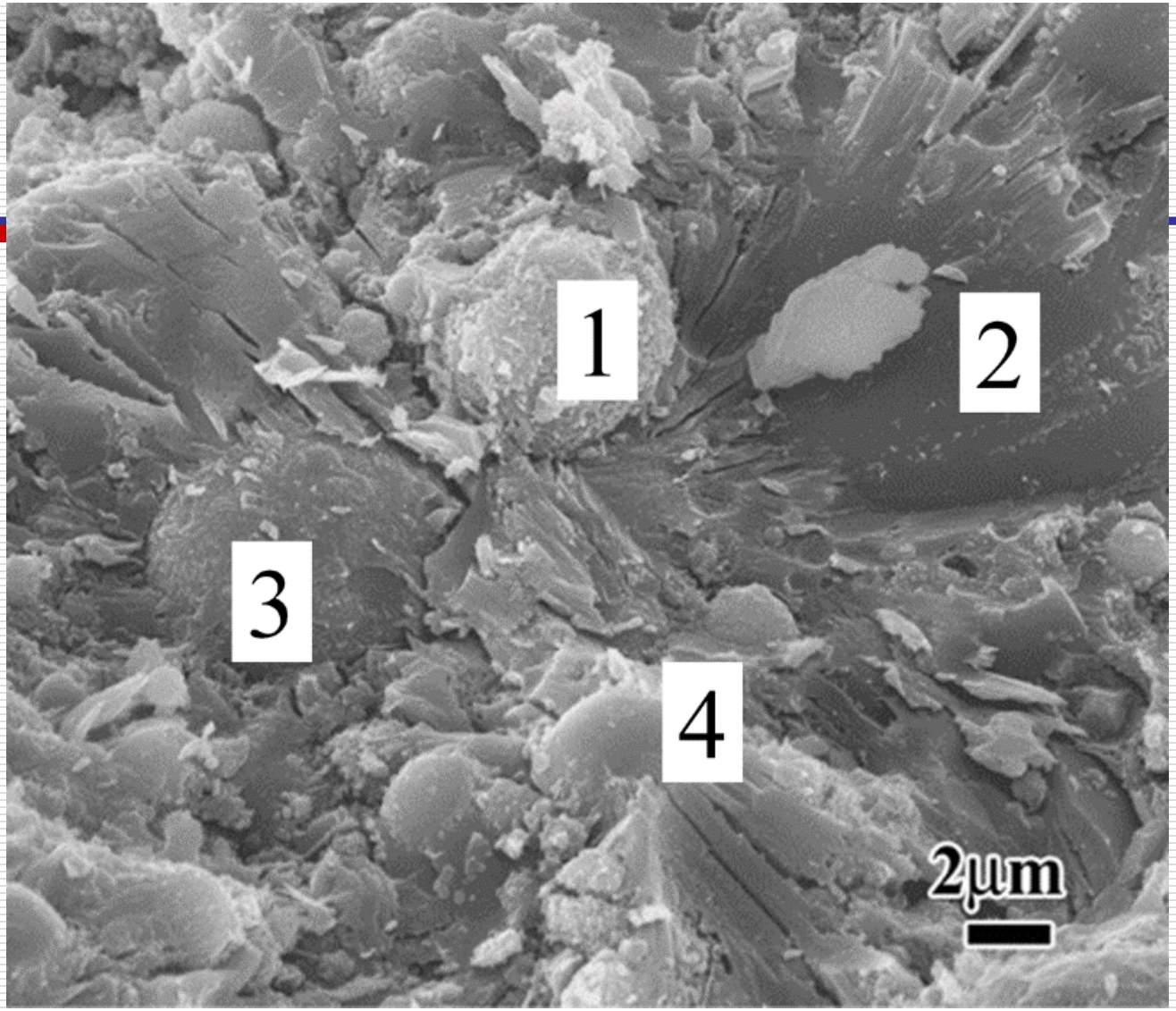

| Element | Wt% | At% |
|---|---|---|
| O | 63.68 | 73.33 |
| Na | 1.85 | 1.48 |
| Mg | 2.59 | 1.97 |
| Al | 4.04 | 2.76 |
| Si | 4.00 | 2.62 |
| P | 0.67 | 0.40 |
| S | 0.90 | 0.52 |
| Ca | 10.56 | 4.85 |
| Ti | 0.93 | 0.36 |
| Fe | 2.62 | 0.86 |
| Sr | 1.25 | 0.26 |
| C | 6.90 | 10.58 |
| **Total** | **100.00** | **100.00** |

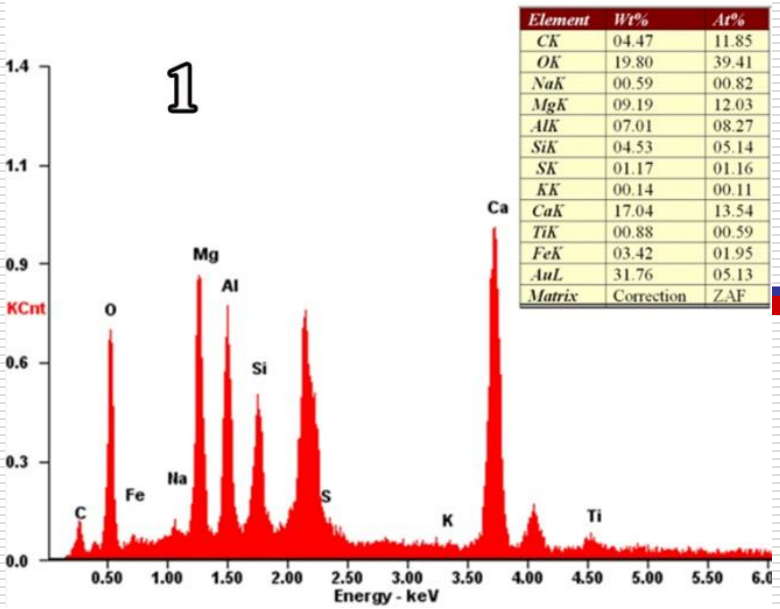
# XRD pattern of fly ash powder and PFAP cured for 1,7, 14, and 28 days



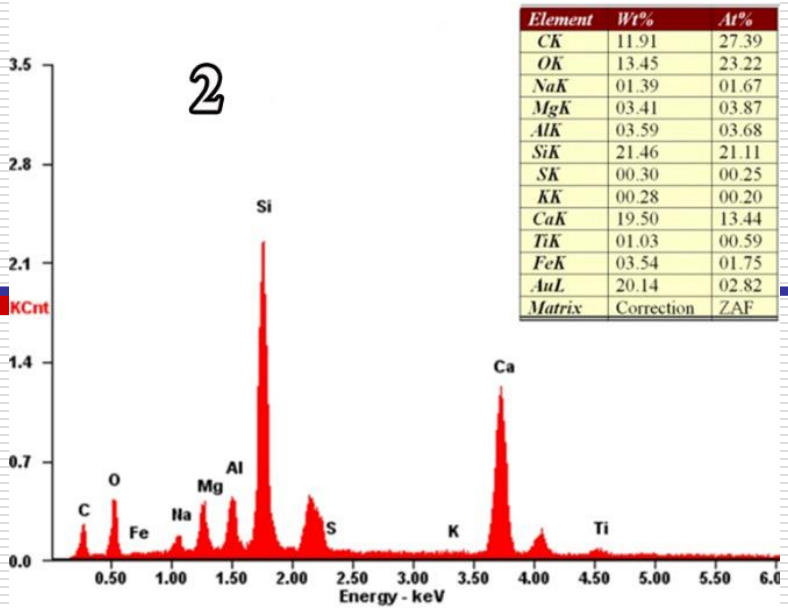
# Compressive strength of the PFAP cured for 1, 3, 7, and 28 days



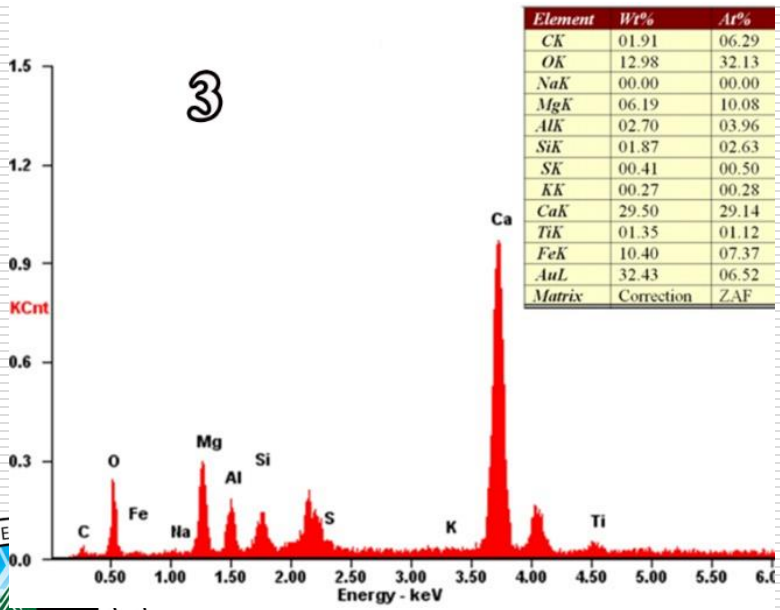

1
2
3
4
2μm



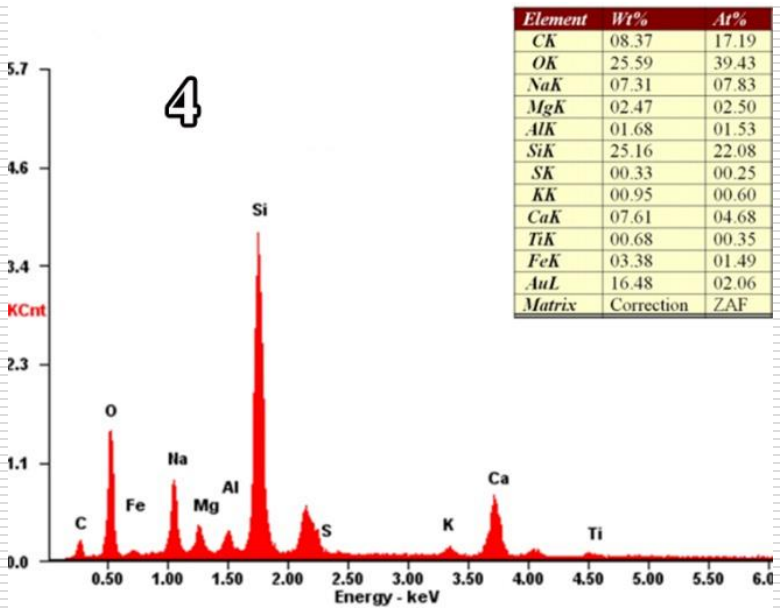

| Element | Wt% | At% |
|---|---|---|
| CK | 04.47 | 11.85 |
| OK | 19.80 | 39.41 |
| NaK | 00.59 | 00.82 |
| MgK | 09.19 | 12.03 |
| AlK | 07.01 | 08.27 |
| SiK | 04.53 | 05.14 |
| SK | 01.17 | 01.16 |
| KK | 00.14 | 00.11 |
| CaK | 17.04 | 13.54 |
| TiK | 00.88 | 00.59 |
| FeK | 03.42 | 01.95 |
| AuL | 31.76 | 05.13 |
| Matrix | Correction | ZAF |



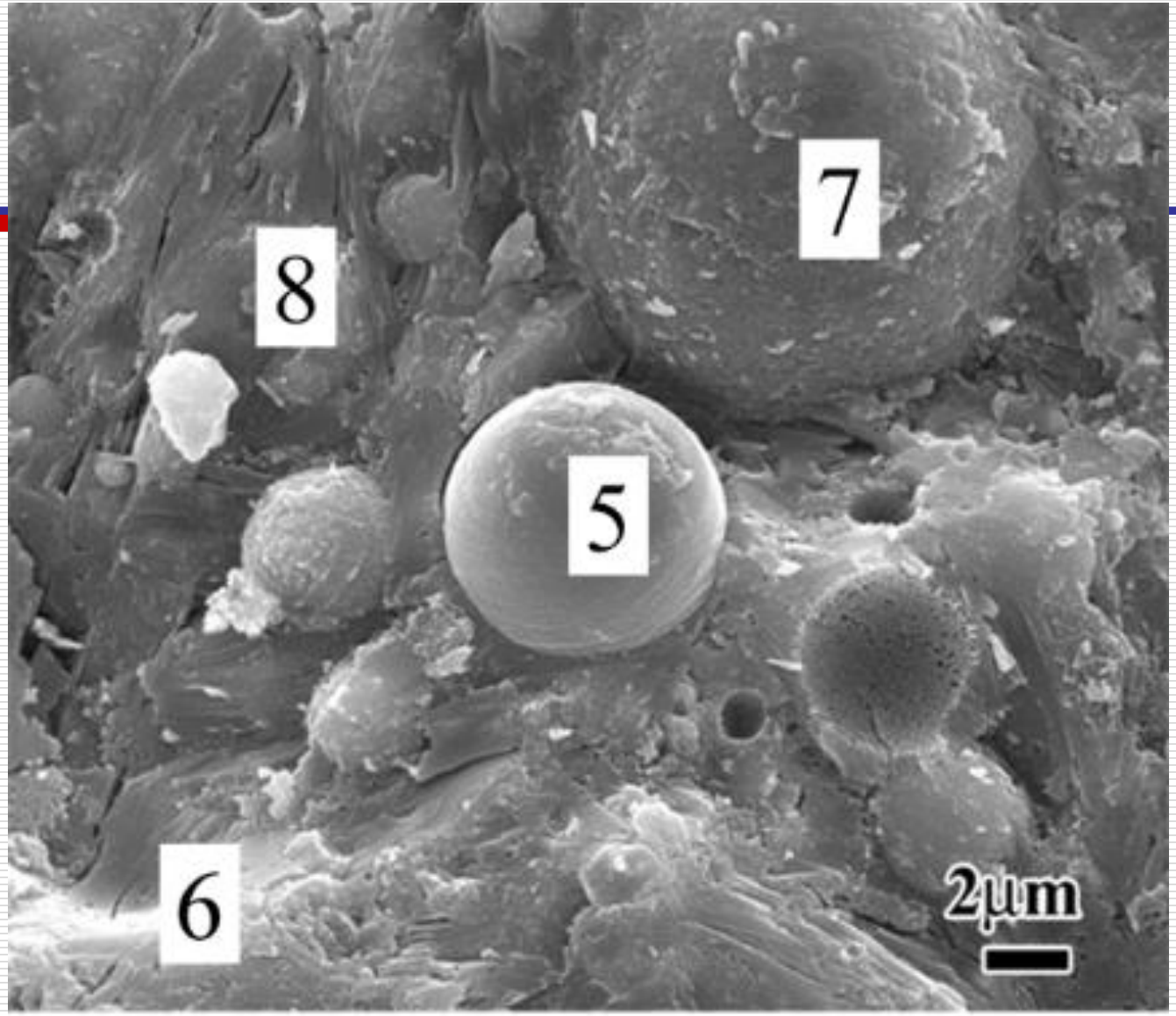

| Element | Wt% | At% |
|---|---|---|
| CK | 11.91 | 27.39 |
| OK | 13.45 | 23.22 |
| NaK | 01.39 | 01.67 |
| MgK | 03.41 | 03.87 |
| AlK | 03.59 | 03.68 |
| SiK | 21.46 | 21.11 |
| SK | 00.30 | 00.25 |
| KK | 00.28 | 00.20 |
| CaK | 19.50 | 13.44 |
| TiK | 01.03 | 00.59 |
| FeK | 03.54 | 01.75 |
| AuL | 20.14 | 02.82 |
| Matrix | Correction | ZAF |

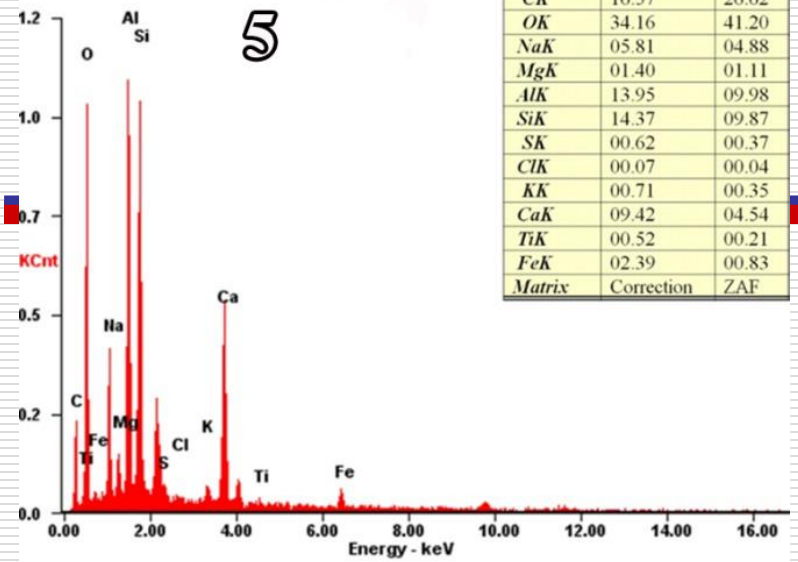



| Element | Wt% | At% |
|---|---|---|
| CK | 01.91 | 06.29 |
| OK | 12.98 | 32.13 |
| NaK | 00.00 | 00.00 |
| MgK | 06.19 | 10.08 |
| AlK | 02.70 | 03.96 |
| SiK | 01.87 | 02.63 |
| SK | 00.41 | 00.50 |
| KK | 00.27 | 00.28 |
| CaK | 29.50 | 29.14 |
| TiK | 01.35 | 01.12 |
| FeK | 10.40 | 07.37 |
| AuL | 32.43 | 06.52 |
| Matrix | Correction | ZAF |

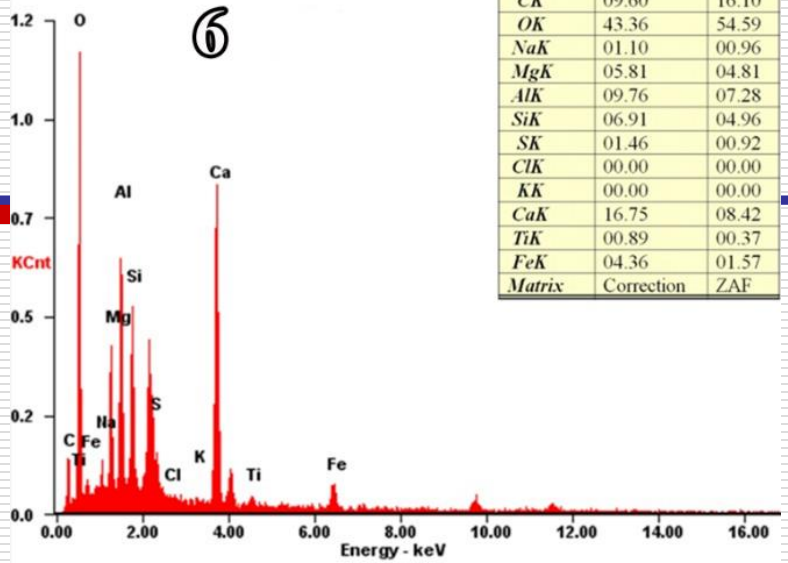



| Element | Wt% | At% |
|---|---|---|
| CK | 08.37 | 17.19 |
| OK | 25.59 | 39.43 |
| NaK | 07.31 | 07.83 |
| MgK | 02.47 | 02.50 |
| AlK | 01.68 | 01.53 |
| SiK | 25.16 | 22.08 |
| SK | 00.33 | 00.25 |
| KK | 00.95 | 00.60 |
| CaK | 07.61 | 04.68 |
| TiK | 00.68 | 00.35 |
| FeK | 03.38 | 01.49 |
| AuL | 16.48 | 02.06 |
| Matrix | Correction | ZAF |

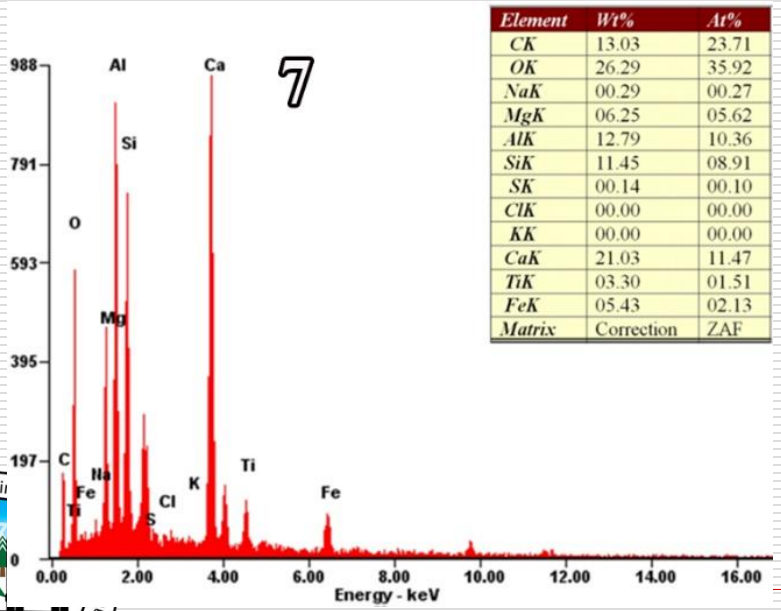

7
8
5
6
2μm



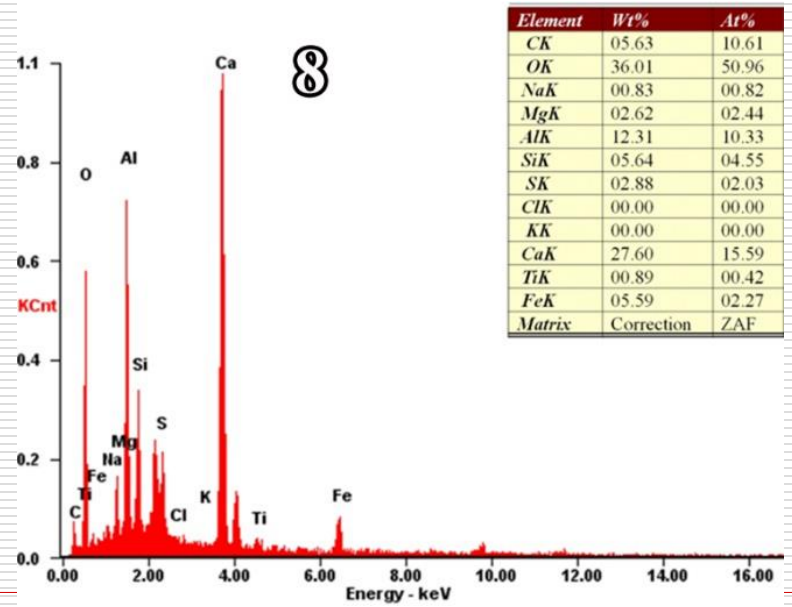

| Element | Wt% | At% |
|---|---|---|
| CK | 16.57 | 26.62 |
| OK | 34.16 | 41.20 |
| NaK | 05.81 | 04.88 |
| MgK | 01.40 | 01.11 |
| AlK | 13.95 | 09.98 |
| SiK | 14.37 | 09.87 |
| SK | 00.62 | 00.37 |
| ClK | 00.07 | 00.04 |
| KK | 00.71 | 00.35 |
| CaK | 09.42 | 04.54 |
| TiK | 00.52 | 00.21 |
| FeK | 02.39 | 00.83 |
| Matrix | Correction | ZAF |



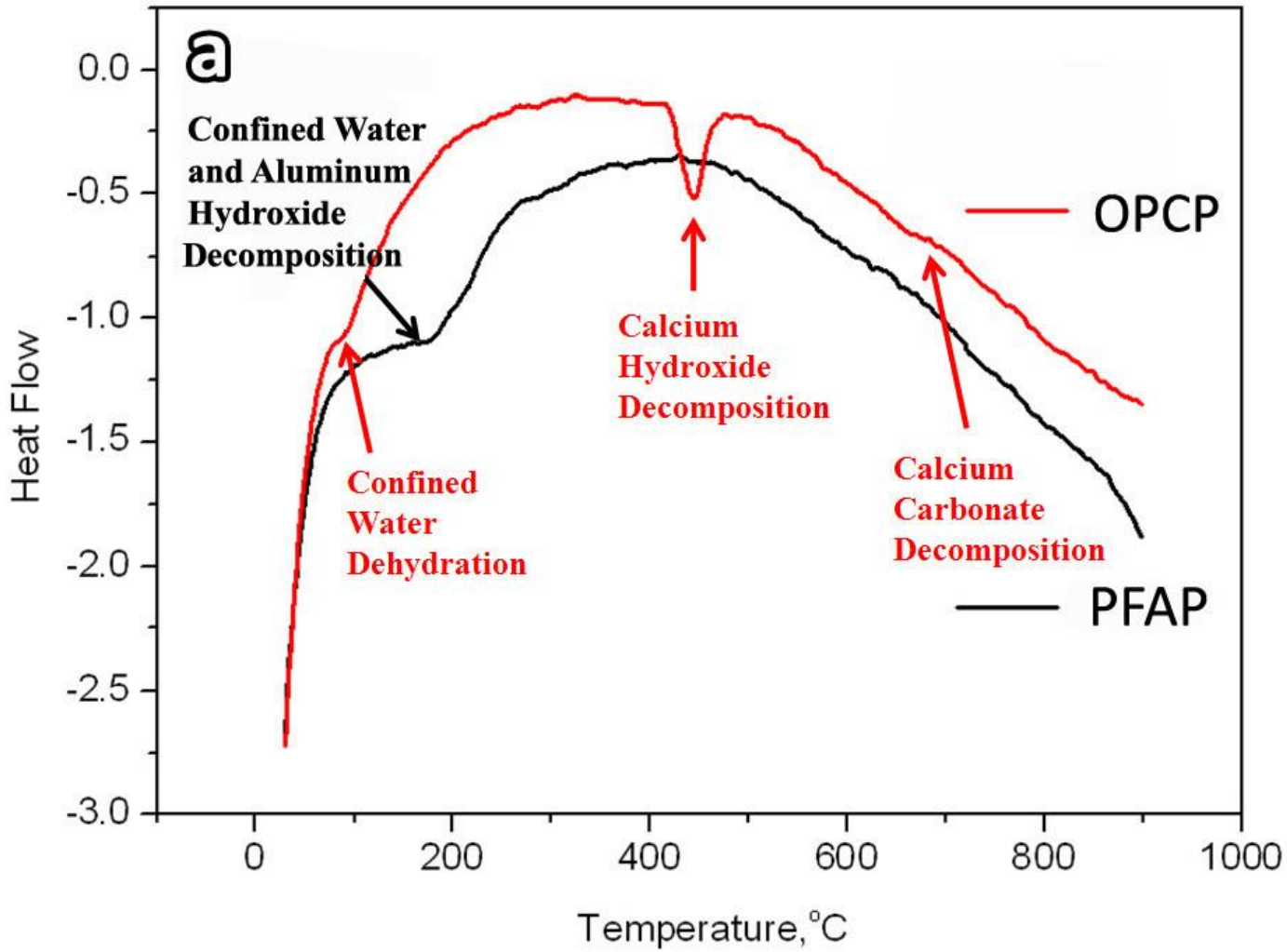

| Element | Wt% | At% |
|---|---|---|
| CK | 09.60 | 16.10 |
| OK | 43.36 | 54.59 |
| NaK | 01.10 | 00.96 |
| MgK | 05.81 | 04.81 |
| AlK | 09.76 | 07.28 |
| SiK | 06.91 | 04.96 |
| SK | 01.46 | 00.92 |
| ClK | 00.00 | 00.00 |
| KK | 00.00 | 00.00 |
| CaK | 16.75 | 08.42 |
| TiK | 00.89 | 00.37 |
| FeK | 04.36 | 01.57 |
| Matrix | Correction | ZAF |



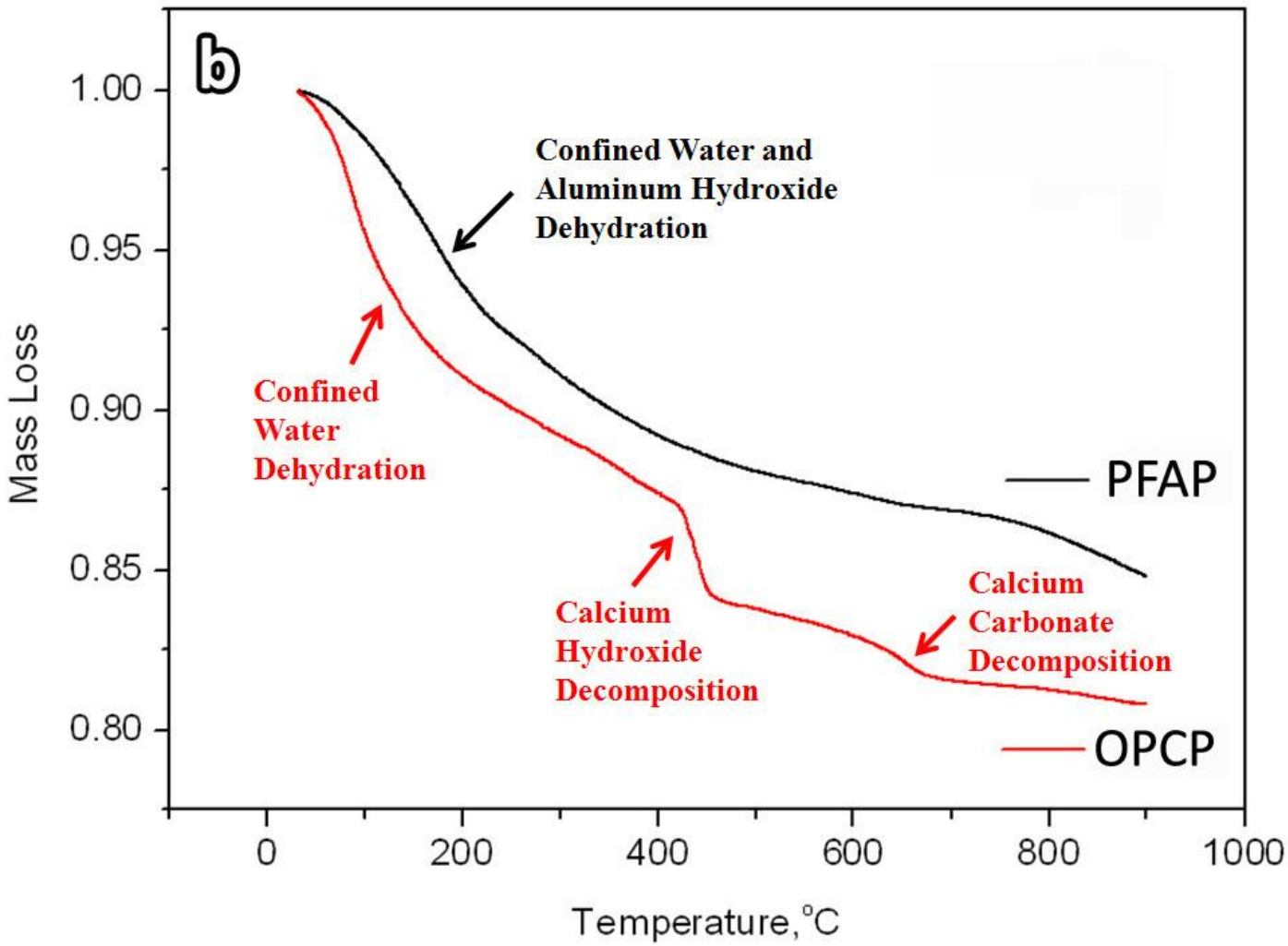

| Element | Wt% | At% |
|---|---|---|
| CK | 13.03 | 23.71 |
| OK | 26.29 | 35.92 |
| NaK | 00.29 | 00.27 |
| MgK | 06.25 | 05.62 |
| AlK | 12.79 | 10.36 |
| SiK | 11.45 | 08.91 |
| SK | 00.14 | 00.10 |
| ClK | 00.00 | 00.00 |
| KK | 00.00 | 00.00 |
| CaK | 21.03 | 11.47 |
| TiK | 03.30 | 01.51 |
| FeK | 05.43 | 02.13 |
| Matrix | Correction | ZAF |




| Element | Wt% | At% |
|---|---|---|
| CK | 05.63 | 10.61 |
| OK | 36.01 | 50.96 |
| NaK | 00.83 | 00.82 |
| MgK | 02.62 | 02.44 |
| AlK | 12.31 | 10.33 |
| SiK | 05.64 | 04.55 |
| SK | 02.88 | 02.03 |
| ClK | 00.00 | 00.00 |
| KK | 00.00 | 00.00 |
| CaK | 27.60 | 15.59 |
| TiK | 00.89 | 00.42 |
| FeK | 05.59 | 02.27 |
| Matrix | Correction | ZAF |




DSC patterns of PFAP and OPCP after cured for 28 days at room temperature with humidity of 95%




TGA patterns of PFAP and OPCP after cured for 28 days at room temperature with humidity of 95%

$$C_3S + 5.3H_2O \rightarrow C_{1.7}SH_4 + 1.3CH \quad (1)$$

$$C_2S + 4.3H_2O \rightarrow C_{1.7}SH_4 + 0.3CH \quad (2)$$

$$C_3S + zC_2S + wH_2O \rightarrow (1+z)C_xSH_y + pCH \quad (3)$$

$$C_3A + 6H \rightarrow C_3AH_6 \quad (4)$$

$$C_3A + 3C\bar{S}H_2 + 26H_2O \rightarrow C_6A\bar{S}_3H_{32} \quad (5)$$

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H_2O \rightarrow 3C_4A\bar{S}H_{12} \quad (6)$$

$$C_4AF + 3C\bar{S}H_2 + 30H_2O \rightarrow C_6A\bar{S}_3H_{32} + CH + FH_3 \quad (7)$$

$$2C_4AF + C_6A\bar{S}_3H_{32} + 12H_2O \rightarrow 3C_4A\bar{S}H_{12} + 2CH + 2FH_3 \quad (8)$$

$$C_4AF + 10H_2O \rightarrow C_3AH_6 + CH + FH_3 \quad (9)$$

$$4CaO + 3Al_2O_3 + SO_3 + 18H_2O \rightarrow 4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O + 2Al_2O_3 \cdot 6H_2O \quad (10)$$

$$4CaO + 3Al_2O_3 + SO_3 + 2CaSO_4 + 38H_2O \rightarrow 6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O + 2(Al_2O_3 \cdot 3H_2O) \quad (11)$$

$$4CaO + 3Al_2O_3 + SO_3 + 6CaO + 8CaSO_4 + 96H_2O \rightarrow 3(6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O) \quad (12)$$

$$Na_2B_4O_7 + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2B_4O_7 \quad (13)$$

# Conclusions

1. The PFAP was successfully prepared at room temperature with an as-received coal fly ash, borax, and with water/binder ratio of 0.2.

2. The hardened pure fly ash paste exhibited a reasonable 28-d compressive strength (36 MPa), rapid strength gain (19MPa and 31 MPa in 1d and 3d, respectively).

3. By characterizing the raw material and PFAP pastes via XRF, SEM/EDS, XRD, and DSC/TGA approaches, the data reveal that the hydration of the CFA is very complex and likely entails reactions between the free Ca2+, Fe3+, Al3+, and Mg2+ and silicates to form amorphous Al-rich and Fe-rich binder phases.