Call 6th Joint Project

ECOFRIENDLY CERAMIC TILE DEVELOPMENT BY GEOPOLYMERIZATION

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July 4-6. 2011
Saint Quentin /France

Call 6th Joint Project

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- Introduction
- Traditional ceramic tile development
- Experimental procedures
    - Geopolymer design parameters
- Result and discussion
- Conclusion

geopolytile by CORNET

AIM OF THE PROJECT

- The objective of this project is to provide the basis for design and construction of energy efficient manufacturing process by transforming the geopolymer technology into the traditional ceramic tile production.

GEOPOLYMER TECHNOLOGY

Activation of reactive alumino silicate materials with high alkali activator (alkali-silicate solutions)

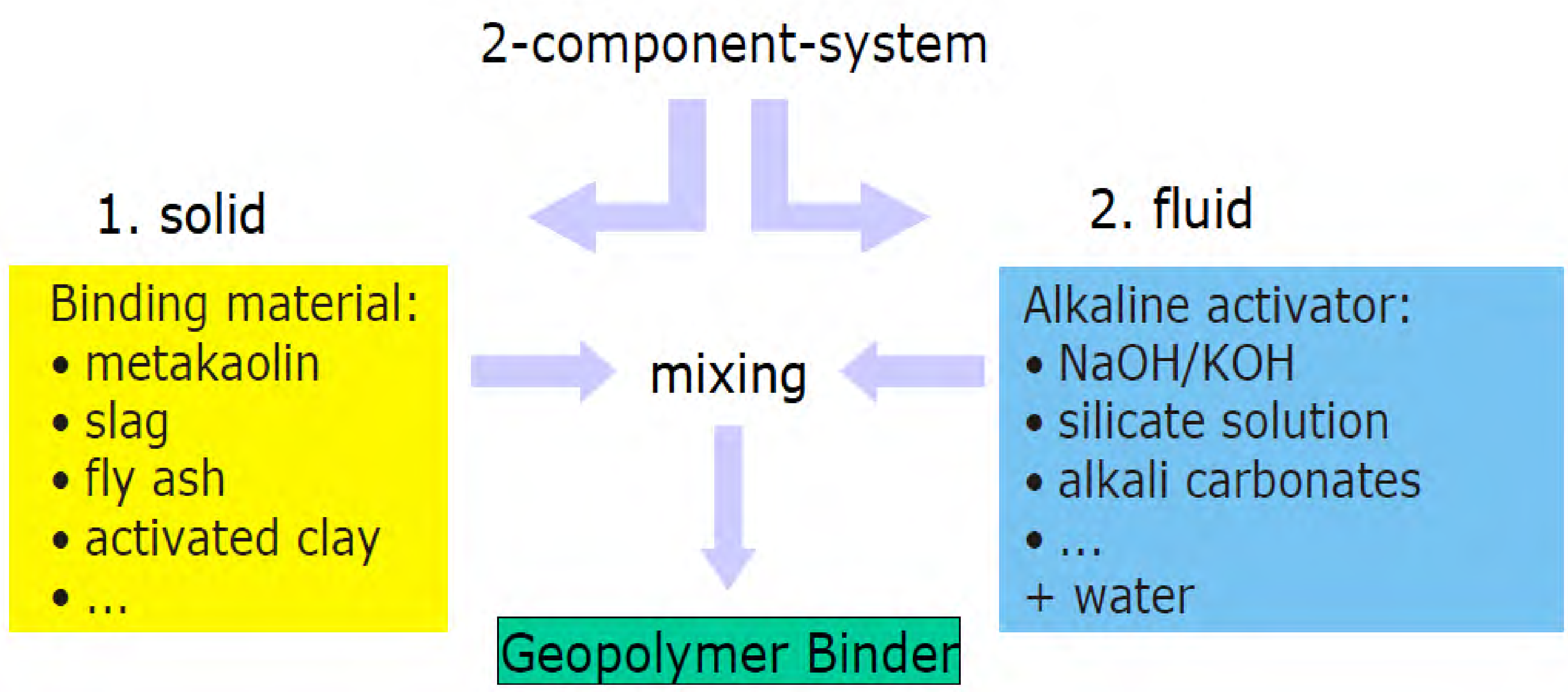


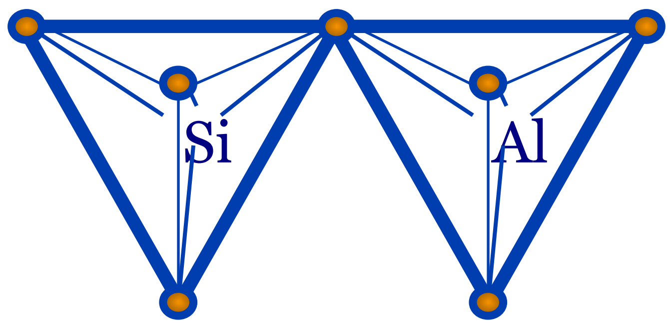
Figure 1.Production steps of geopolymers

New state of art materials designed with the help of geopolymerization reactions are opening up new aplications :

- High temperature techniques are no longer necessary to obtain materials which are ceramic-like in their structures and properties.

- These materials can polycondense just like organic polymers, at temperature lower than 100°C.

- Geopolymerization involves the chemical reaction of alumino-silicate oxides with alkali polysilicates yielding poliymeric Si-O-Al bonds → the amorphous to semicrystalline three dimensional silico-aluminate structures.



Traditional Ceramic Tile Production

Raw Material Preparation

↓

Milling& Homogenization

↓

Spray Drying (Granulation) → **Dry Granulation**

↓

Shaping (Pressing)

↓

Firing & Glazing (1100 – 1250^{o}C)

Figure 2. General process flow diagram

<u>Basic raw materials</u>

- Clay, Kaolin, Quartz, Feldspar, Calcite, Dolomite

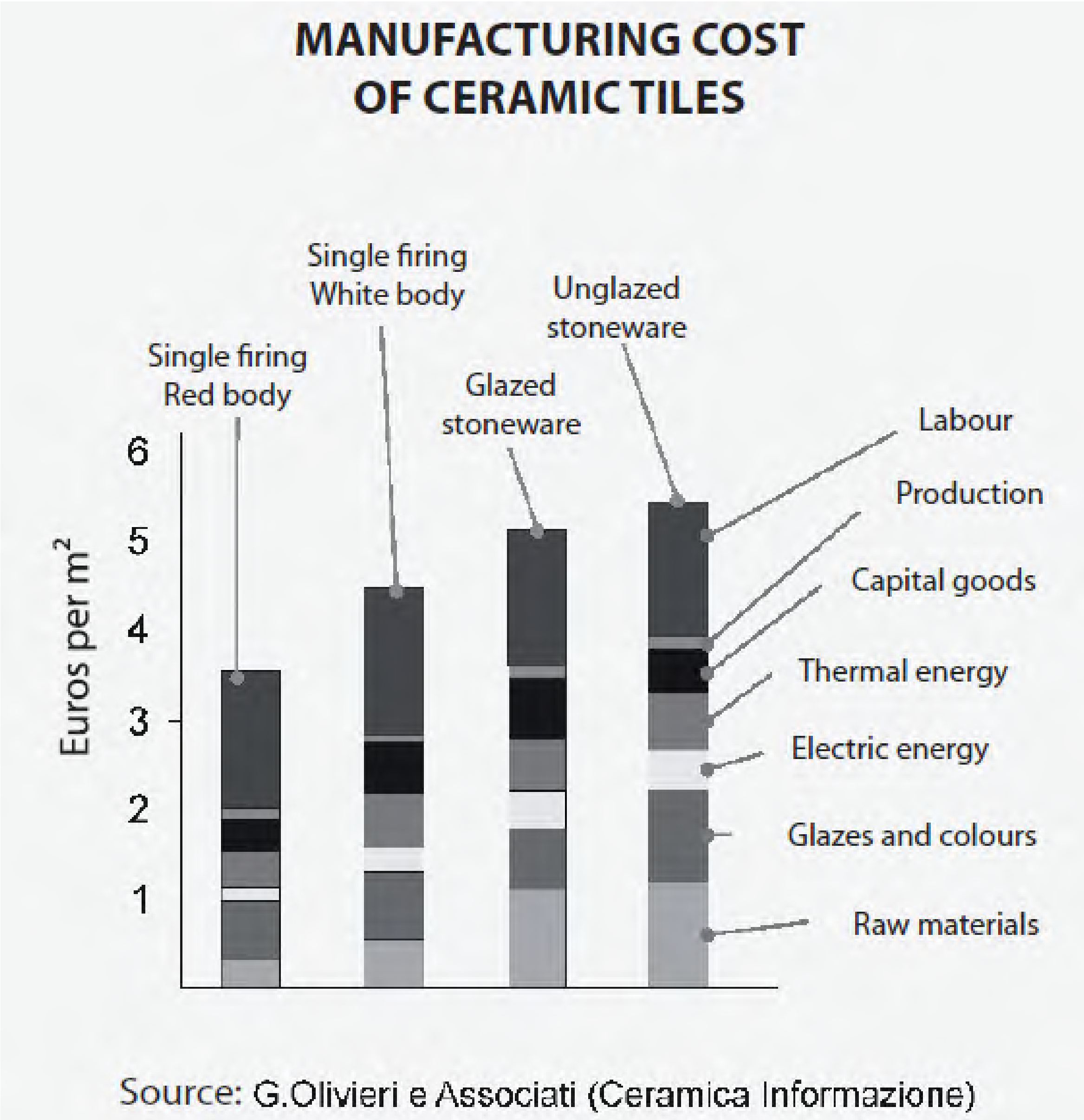


Figure 3. Diagram of approximate cost split for different types of ceramic tile, where, apart from employment, the greatest costs relate to raw materials, glazes and colours, which indicates where cost saving strategies should be focused.

Energy cost is a significant percentage of the total production costs; around 30-35%

Drying and firing stage use **65 %** of the total process energy

L. Sánchez-Muñoz, I.T. Marinova, G.F. de la Fuente,I. Núñez, M.A. Rodríguez, J. Sanz, J.B. Carda; "R&D+i for ceramic tiles in the 21st century: Competition, divercity, and functionality; Qualicer 2010

Tile Production

Emissions

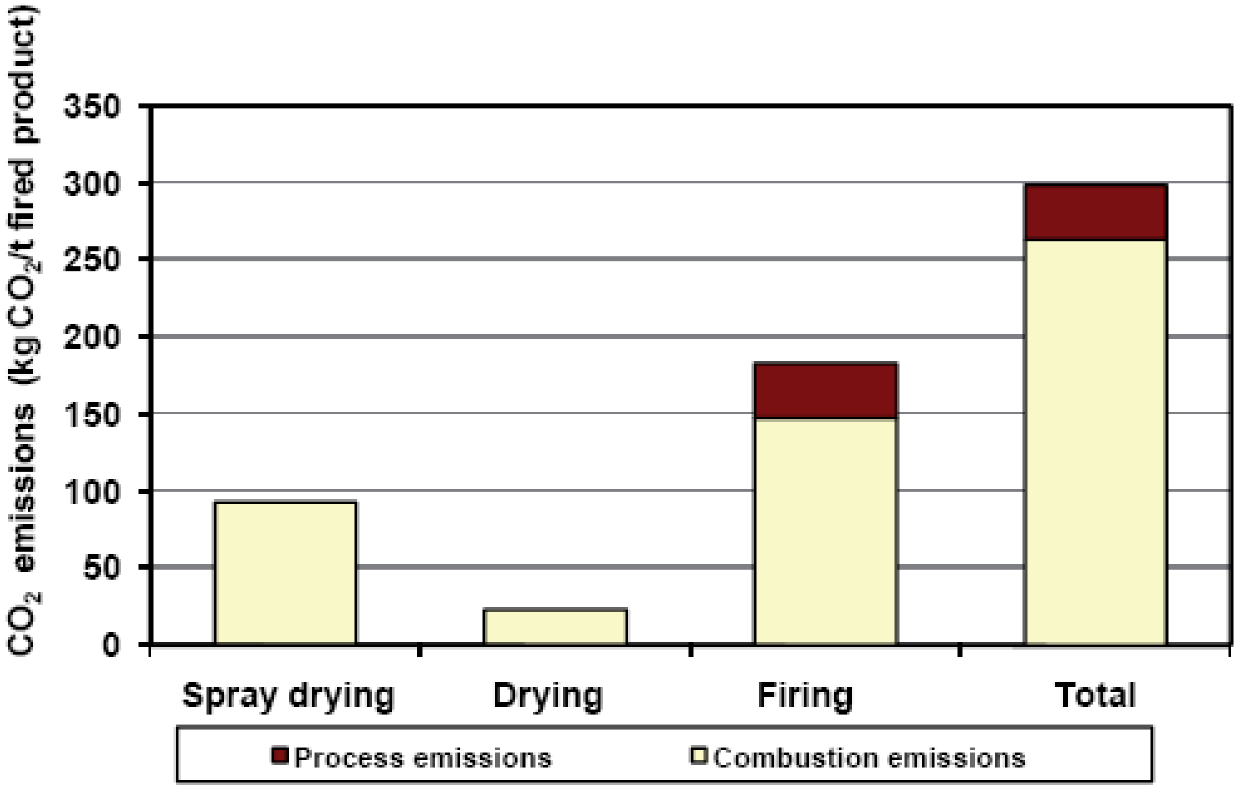


Figure 4. Average CO_2 emissions (steady-state operation).

CO_2 emission

- 0.25 kg CO_2 / kg final product
- 3 kg CO_2 / m^2 final product

Monfort, A. Mezquita, R. Granel, E. Vaquer, A. Escrig A. Miralles, V. Zaera; "Analysis of energy consumption and carbon dioxide emisions in ceramic tile manufacture"; Qualicer 2010

Prospects of Geopolymerization

- **Energy saving:** Geopolymers harden under normal climatic conditions and need no high temperature heat treatment. Therefore, the potential of energy saving is substantial (drying and firing steps use around 65% of the total ceramic process energy).

- **Alternative raw materials**: Generally a wide range of raw materials is possible to be employed, beside highly pure metakaolins different meta-clays as well as industrial by-products such as fly ashes are usable.

- **Reduction of CO_2 emission:** By using geopolymers which harden at lower temperatures (25-150°C), it is possible to reduce CO_2 emission remarkably

Geopolymer

Metakaolin based Geopolymer; Poly(sialate-siloxo), Si:Al =2:1

The method for making (Na,K)PSS comprises preparing a Na- silico aluminate / K- silico-aluminate water mixture where the oxide mole ratios falls within the range :

Oxide-Mole Ratios of the Reactant Mixture	
SiO_2/Al_2O_3	3,5 – 4,5
$(Na_2O+K_2O) / SiO_2$	0,2 – 0,28
$(Na_2O+K_2O) /Al_2O_3$	0,8 – 1,2
$H_2O / (Na_2O+K_2O)$	15 – 17,5

Higher ratios induce a free alkalinity in the solidified polymer and cause alkali silicate migration, which can disturp the mechanical properties of the resulting material.

EXPERIMENTAL STUDY

COMPONENTS

- Sources of silica and aluminum
  - Metakaolin (CC-31 and K-413)
    - Dehydroxylated kaolinite (Calcination 750^{o}C/10h)

      $2(Si_2O_5 \cdot Al_2(OH)_4)_n \rightarrow 2(Si_2O_5 \cdot Al_2O_2)_n + 4n\ H_2O$
  - Filler
    - Quartz, perlite, bentonites
- Alkaline Activator
  - Alkali hydroxide or alkali silicate solution
  - Usually Na, K (Na-hydroxide preferred)

GEOPOLYMER DESIGN FOR PRESSING

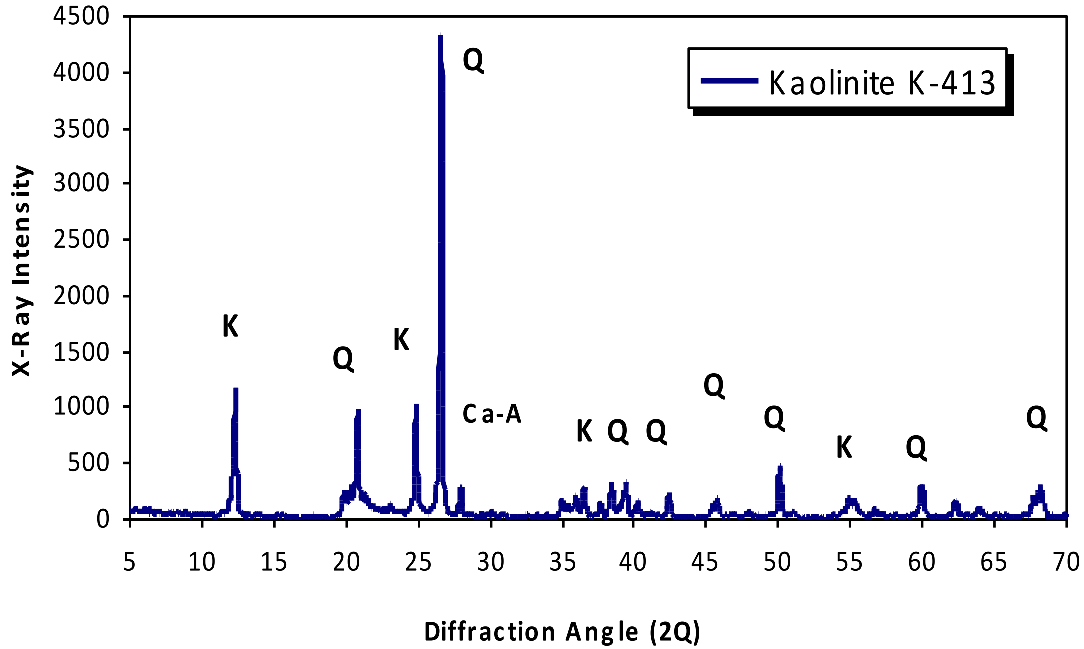
EXPERIMENTAL STUDY

Material Chracterization

Raw Materials	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I
K-413 Kaolinite	69,57	20,47	0,32	0,45	0,28	0,10	0,22	0,17	7,99
Perlite	72,802	12,610	0,142	0,904	0,751	0,178	3,814	4,979	3,821

Table 1. Chemical composition of the starting raw materials (wt%).

Minerological analysis



Q : Quartz (SiO_2)
K: Kaolinite ($Al_2O_3.2SiO_2$)
Ca-A: Ca-Albite
I : Illite

Table 2. The quantitative phase analysis were made by applying Rietved Method

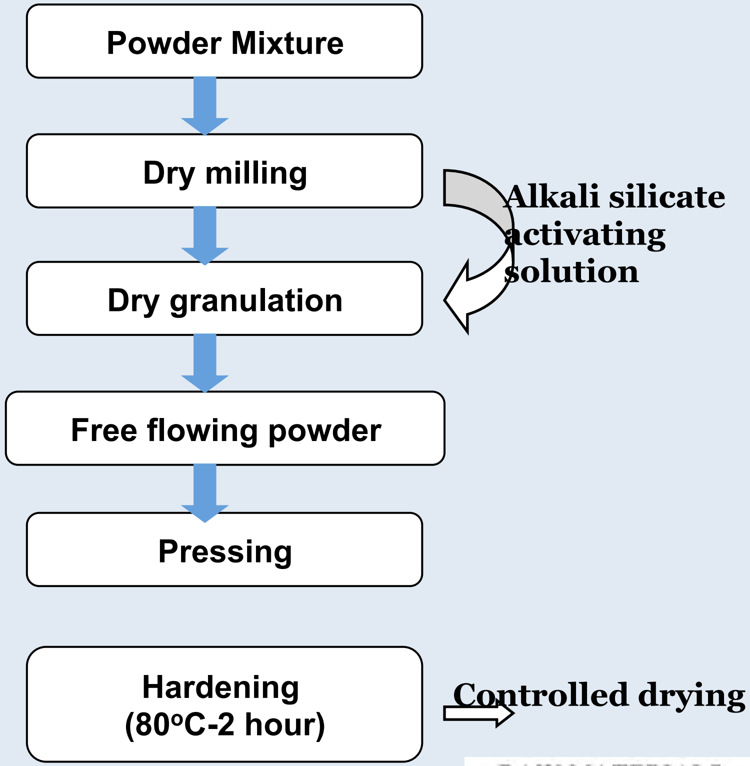
Raw Materials	Kaolinite (%)	Quartz (%)	Illite (%)	Ca-Albite (%)
K-413 Kaolinite	46,05±0,56	48,33±0,62	0,91±0,16	4,69±0,26

Reactive oxides from kaolinite :

	Chemical analysis (%)		Minerological analysis (%)		$Al_2O_3.2SiO_2.2H_2O$ 1 moles = 258gr		
Raw Materials	SiO_2	Al_2O_3	Kaolinite	Quartz	SiO_2	Al_2O_3	H_2O
K-413 Kaolinite	69,57	20,47	46,05	48,33	46,51	39,05	13,95

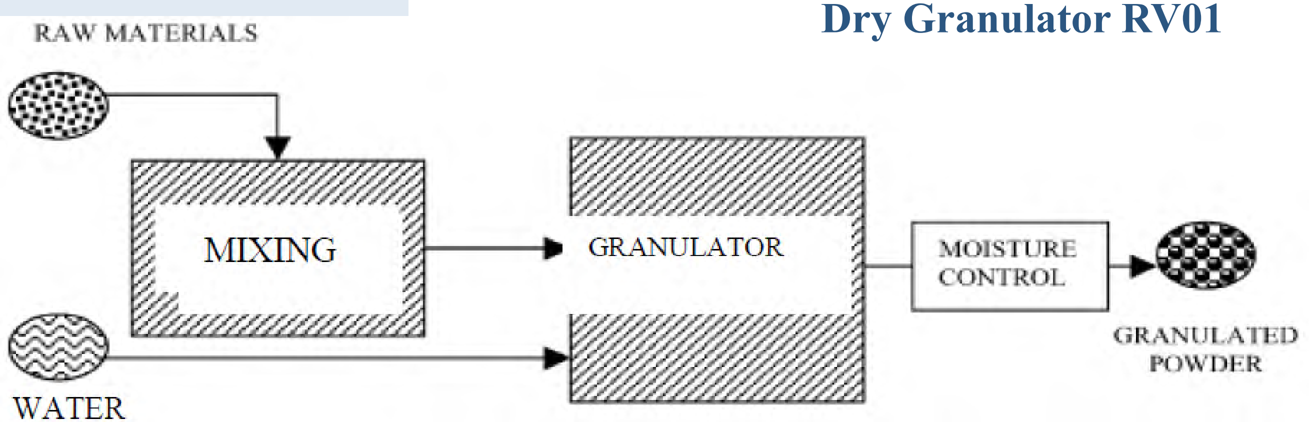
The reactive oxides from kaolinite (wt%)			Free Quartz (wt%)	Molar Ratio
	SiO_2	Al_2O_3		SiO_2/Al_2O_3
K-413	21,4	17,98	48,33	2,03

THE EXPERIMENTAL STUDY : Process



Process flow diagram

Dry Granulator RV01



Dry granulation process

Granule shape, morphology and flow behaviour

The flowability check of dry-granulated metakaolin-quartz based geopolymer compositon. Granulated by alkali activating solution (J-MQ-Na).

Angle of rest method $\alpha_1 = 30^o$

THE EXPERIMENTAL STUDY : Compositions

Raw materials	K-413 Kaolinite	Quartz	Bentonite
J-MQ-Na	25 %	70 %	5 %

2kg batch / 500 gr K-413

Sprey- Alkaline solution :

%14 humidity before pressing

Heat treatment : 80^{o}C / 2h.

Flextural strength (7 days) : 17-18 MPa

Immersed in water for 3 days : **No Dissolution**

SiO_2 / Al_2O_3 = 3,99

Na_2O / SiO2 = 0,29

Na_2O / Al_2O_3 = 1,18

H_2O / Na_2O = 15-16

THE EXPERIMENTAL STUDY : Compositions

Raw materials	K-413 Kaolinite	Perlite	Bentonite
J-PM	25 %	70 %	5 %

2kg batch / 500 gr K-413

Alkaline solution :

%14 humidity before pressing

Pressing : 125bar (450kg/cm^{2})

Heat treatment : 80^{o}C / 2h.

Flextural strength (7 days) : 17-18 MPa

Immersed in water for 3 days : **No Dissolution**

SiO_2 / Al_2O_3 = 7,6

Na_2O / SiO_2 = 0,2

Na_2O / Al_2O_3 = 1,5

H_2O / Na_2O = 12

Mechanical properties : Flextural Strength

	Flextural strenght (MPa)				
Compositions	Hardening	7 Day	28 Days	7day + 650°C	Boiling test (2h boiling)
J-MQ-4-Na	80°C / 2h.	18,19	19,82	23,35	17,96
J-PM	80°C / 2h.	17,87	18,47	22,53	16,85

Breaking load: This test is conducted according to the method described in standard EN ISO 10545-4: 1997 “Ceramic tiles - Part 4: Determination of modulus of rupture and breaking strength”

Min. flextural strenght for wall tiles : 12-15 MPa

Determination of the soundness of geopolymer specimens

Standart boiling water tests:

The Sample J-MQ-Na	Bending strength
Early strength at 7 days	17-18 MPa
After kept in a water bath for 24h at 18-22°C.	15-16 MPa
After boiled in a water for 2h	13-14 MPa
After kept in a water bath for 24h at 18-22°C / Early strength at 7 days (16/18) = **0,88** After boiled in a water for 2h / Early strength at 7 days **(14/18= 0,78** The samples free of crack after boiling test.	

The hardened geopolymer samples were put for 1h in boiling water. There is no dissolution or destruction for the J-MQ-Na and J-PM geopolymer samples

Thermal behaviour, expansion at 250°C, thermal dilatometry :

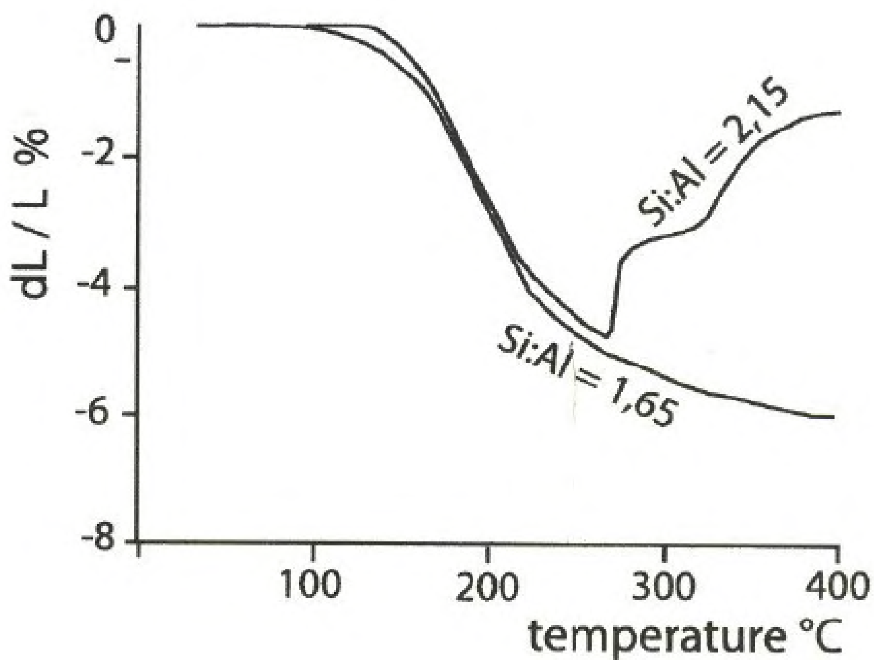
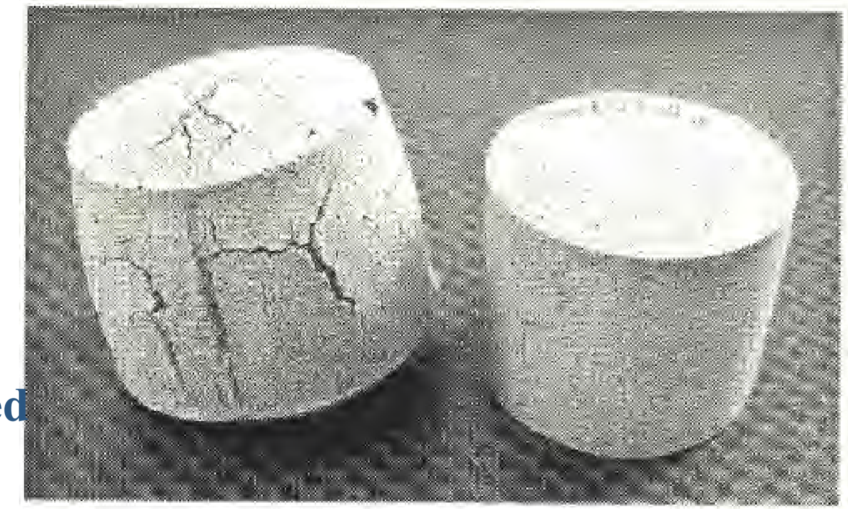


Figure 5. Dilatometrical curves of fully condensed (Si:Al =1,65) and non-fully condensed (Si:Al =2,15) geopolymers.



Heat treatments at 250°C; left, not-fully condensed geopolymer, expansion; right, fully condensed, no expansion

Thermal behaviour, expansion at 250ºC, thermal dilatometry :

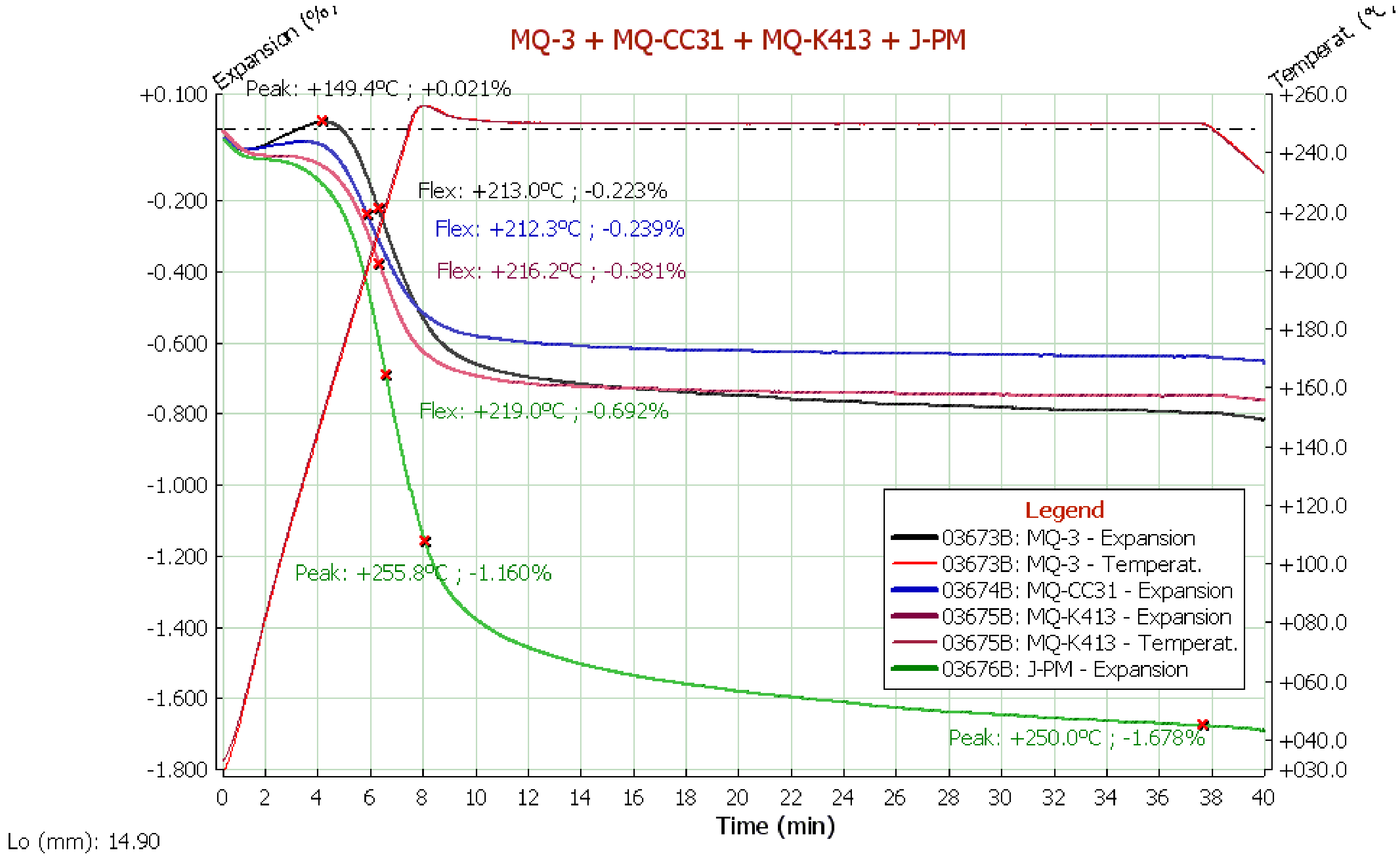


Figure 6. Thermal behaviour of the geopolymer samples (50ºC/min. up to 250ºC with 30min. dwell time)

Microstructure

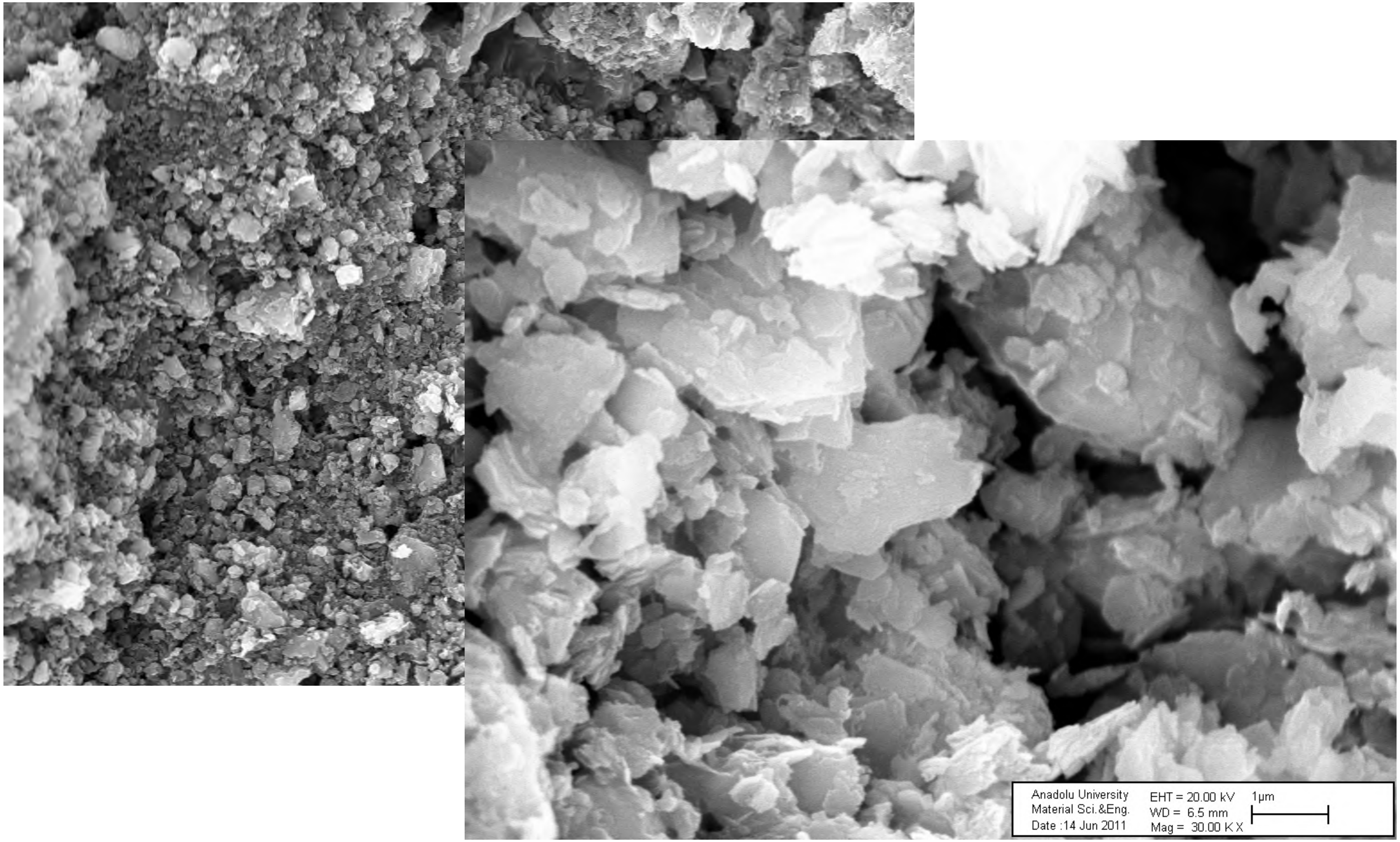


Figure 7. Typical SE images taken from the fractured surface (J-MQ-Na)

Microstructure

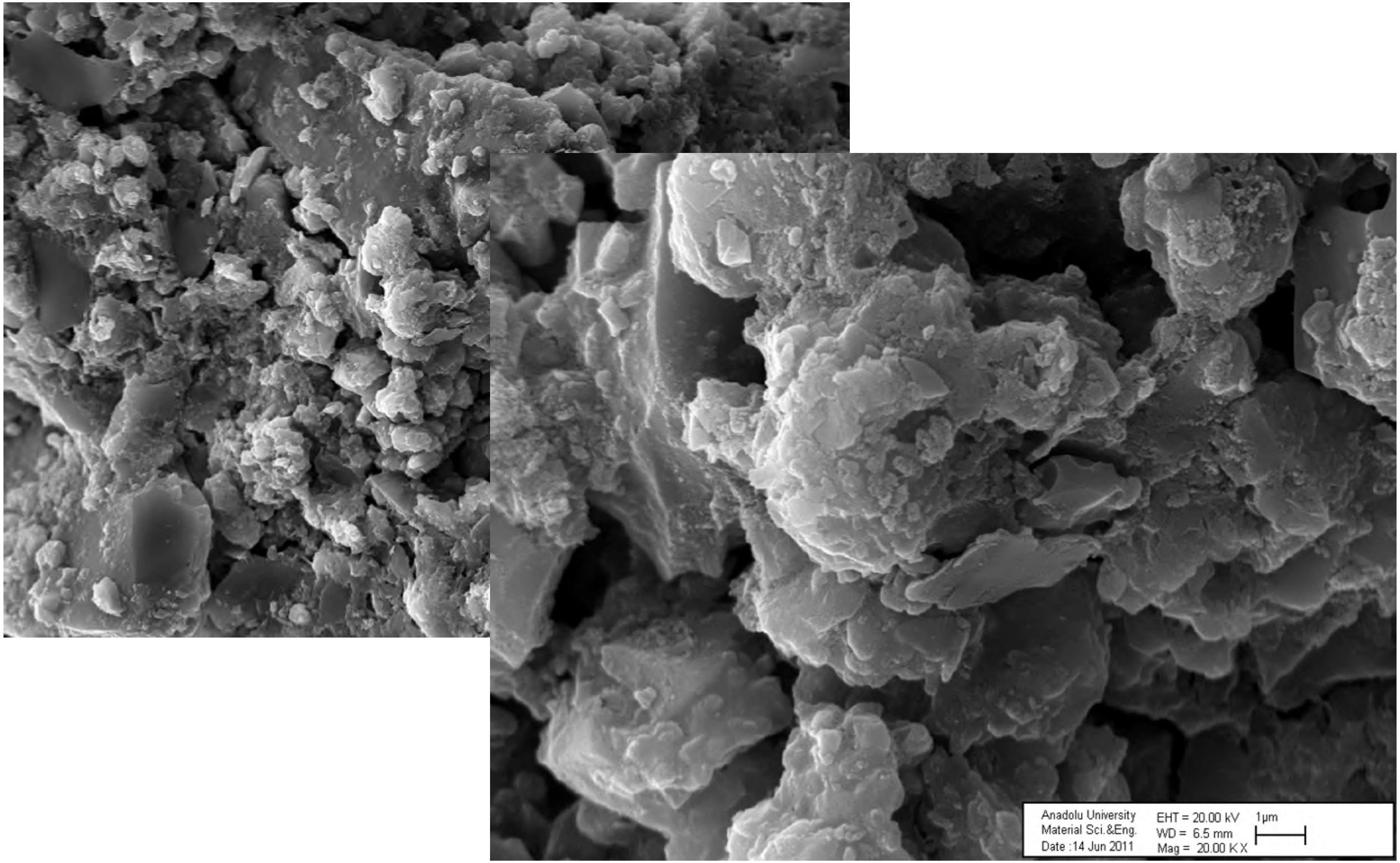


Figure 8. Typical SE images taken from the fractured surface (J-PM)

CONCLUSION

- Energy efficient manufacturing process were developed by transforming the geopolymer technology into the traditional ceramic tile.
- Geopolymer materials that can be shaped by powder pressing and hardens without a high temperature treatment were developed.
- This new processing method is expected to have immediate applications in the ceramic tile industry, where raw material and fuel costs are significant.

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Thanks!!!

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