

Presented as a poster at the 12<sup>th</sup> International Ceramic Congress CIMTEC 2010, June 6-11 2010, Montecatini Terme

## Geopolymerization of meta-kaolins with different morphologies

J. Dedeczek<sup>1</sup>; V. Medri <sup>\*2</sup>, S. Fabbri <sup>2</sup>; Z. Sobalik<sup>1</sup>, Z. Tvaruzkova<sup>1</sup>; A. Vaccari <sup>3</sup>

<sup>1</sup> J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 2155/3, 18 223, Prague 8, Czech Republic

<sup>2</sup> ISTECCNR, Via Granarolo 64, 48018 Faenza, Italy

<sup>3</sup> Dipartimento di Chimica Industriale e dei Materiali, Alma Mater Studiorum –University of Bologna, Viale Risorgimento 4, 40136, Bologna, Italy

**Abstract:** The reactivity of two commercial meta-kaolins with similar composition and specific surface areas but different morphologies was tested during geopolymerization with potassium silicate alkaline solution. Manual and short term mechanical stirrings were used to not complete geopolymerization and to emphasize the powders surface reactivity. Moreover, radiation, infra red, micro waves heating were used during curing. The degree of geopolymerization was checked by SEM and N<sub>2</sub> adsorption (BET), FTIR and <sup>27</sup>Al MAS NMR spectroscopies. The meta-kaolin powder with rounded agglomerates was the less reactive, but it was the more sensitive to the various geopolymerization conditions. The fine dispersed lamellar powder was more reactive and it was mainly affected by mixing. The addition to the potassium silicate alkaline solution of a small alkaline cation such as lithium favoured the dissolution stage during geopolymerization, but decreased the melting temperature.

# ROLE OF THE METAKAOLIN MORPHOLOGY ON GEOPOLYMERIZATION

V. Medri<sup>1</sup>, S. Fabbri<sup>1</sup>, J. Dedecek<sup>2</sup>, Z. Sobalik<sup>2</sup>, Z. Tvaruzkova<sup>2</sup>, A. Vaccari<sup>3</sup>

<sup>1</sup> ISTE-CNR, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, 48018 Faenza, Italy

<sup>2</sup> J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 2155/3, 18 223, Prague 8, Czech Republic

<sup>3</sup> Dipartimento di Chimica Industriale e dei Materiali, Alma Mater Studiorum - Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italy

## In brief

Two commercial metakaolins were tested during partial geopolymerization with potassium silicate in order to emphasize the different surface reactivities. Both manual and short term mechanical stirring were used during slurries preparation, while radiation, infrared and micro waves heating were used during curing.

The metakaolins had similar compositions and specific surface areas, but different morphologies and dehydroxylation degrees deriving from different calcination kilns technologies.

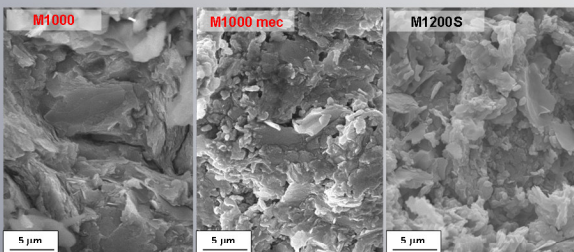
The degree of geopolymerization was checked by <sup>27</sup>Al MAS NMR spectroscopy. Moreover, ionic exchange in geopolymers by CsNO<sub>3</sub> and Co(NO<sub>3</sub>)<sub>2</sub> was applied to monitor accessibility of geopolymer inner volume. Only networked tetrahedral aluminium exhibit ion exchange properties. Thus, charge balance (sum of the extraframework cations balancing Al) can be used as a measure of geopolymerization in the network.

Besides the different dehydroxylation degrees the metakaolins had similar reactivity. The metakaolin powder with rounded agglomerates and with lower water demand was more sensitive to the various geopolymerization conditions than the fine dispersed lamellar one, giving rise to very different micro and macrostructures of the partially geopolymerized samples. IR heating seemed to slightly increase the geopolymerization degree, while MW heating induces the fast evaporation of the water forming porous samples.

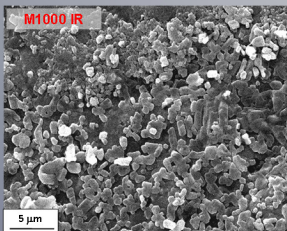
## Samples preparation

The molar ratios are SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=4 and Al<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O=1. Geopolymer samples were prepared by manual mixing or mild mechanical mixing (mec) at 10 r.p.m. After 5 min of mixing the slurry was transferred into polyethylene moulds, which were sealed. After a maturation at room temperature, the samples were cured in a laboratory heater (radiation heating), infrared (IR), furnace and microwaves (MW) oven up to 80°C.

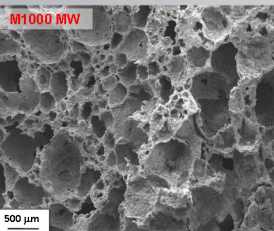
### Radiation heating



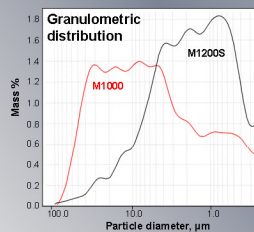
### Infrared furnace



### Microwaves

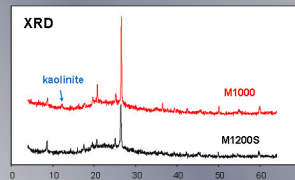
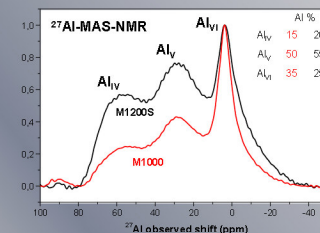
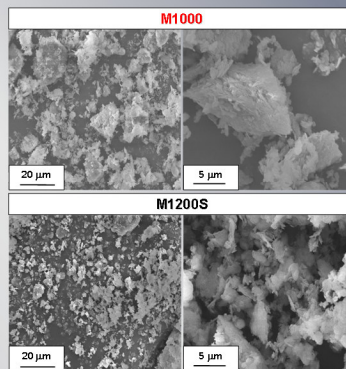


## Metakaolins characterization



Characteristics of the two metakaolins from the technical data sheet of the producer, AGS Mineraux, Clérac, France.

Brand name	s.s.a (m <sup>2</sup> /g)	Chemical analysis (%)							Water Demand Marsh cone (g/kg)	Bulk density (kg/m <sup>3</sup> )	Calcining kiln
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O Na <sub>2</sub> O	CaO	MgO			
M1000	17	40.0	55.5	1.4	1.5	0.8	0.3	900	400	Rotary	
M1200S	19	39.0	55.0	1.8	1.5	1.0	0.6	1650	250	flash	



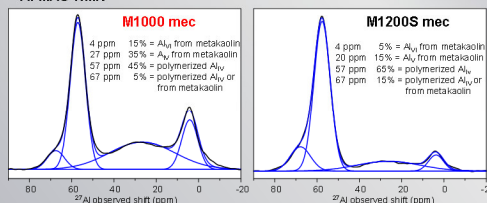
## Geopolymers characterization

### Ion exchange capacity and degree of geopolymerization

	M1000	M1200S	M1000IR	M1200SIR
Geopolymerization degree* (Cs+K+Na)/Al %	24	26	26	25
Geopolymerization degree** (Z <sup>2+</sup> Co+K+Na)/Al %	17	20	21	22

\* Geopolymerization degree calculated from maximum Cs ion exchange  
 \*\* geopolymerization degree calculated from maximum Co(II) ion exchange

### <sup>27</sup>Al-MAS-NMR



Sample	Geopolymerization degree*** (%)
M1000	35± 5
M1200S	45± 5
M1000 IR	45± 5
M1200S IR	50± 5
M1000 mec	45± 5
M1200S mec	65± 5

\*\*\*Degree of geopolymerization calculated as ratio of Al with resonance at 57 ppm to the total intensity of <sup>27</sup>Al spectrum

## Discussion

M1000 has rounded massive aggregates of lamellar particles with a D50= 6.5; M1200S is composed by fine lamellar particles with low agglomeration and D50=1.7.

It is important to use metakaolin where the penta-coordination of Al (-Al=O) is maximized, as it is the most reactive in alkaline conditions (Davidovits, 2008). For Both M1000 and M1200S the NMR spectra show the dehydroxylation is not complete as between the three lines belonging to Al in VI, V and IV coordination, the Al (VI) line belonging to the starting kaolin is the most intense. XRD analyses show that M1000 still contained traces of original kaolinite. For this reason the reactivity of the two metakaolins is expected to be quite low.

As the calcination range was the same for both the metakaolins, the kiln technology greatly affect both the resulting morphologies and the dehydroxylation and consequently the reactivity of the metakaolins (Davidovits, 2008).

The morphology rich of hard agglomerates and the lower dehydroxylation degree made M1000 less reactive. After the curing treatment in heater no clear presence of geopolymeric precipitates is found in the microstructure, moreover the porosity is very low due to the presence of residual water. The mild mechanical mixing helps geopolymerization, homogenising the slips and renewing the reactive surface of the powders.

The heating systems influence the micro- and macro- structures. IR induces the formation of rounded particles with diameter <1 µm and an almost complete water removal. MW at 80 W induces the formation of macro-porous samples, due to the fast evaporation of water. This foaming effect is not observed on mechanical mixed samples stating the effectiveness of the mechanical stirring to promote the geopolymeric reaction. Concerning M1200S, no relevant microstructural differences are revealed between samples from manual or mild mechanical mixing and from different curing conditions.

The concentration of extranetwork cations in the geopolymer can be used as a measure of Al incorporated to geopolymer network. Geopolymerized Al exhibits tetrahedral coordination and in the network of tetrahedral Si atoms bears negative charge, which has to be balanced by extranetwork cation. As expected for partially geopolymerized samples, that majority of Al atoms in geopolymer is not balanced by extranetwork cations. Thus, significant part of Al atoms in both M1000 and M1200S metakaolins was not transferred to tetrahedral network of geopolymer and balanced by extranetwork cations and geopolymerization degree from Cs exchange results to be around 25% for samples from both the metakaolins. The lower ion exchange capacity of Co exchanged geopolymer results from proton exchange to geopolymer from acidic Co nitrate solution. However Co exchange seems to be more sensitive to underline the difference between the reactivity of the two metakaolins and/or the effect of the curing and mixing method.

<sup>27</sup>Al MAS NMR spectra exhibited resonance around 3, 28, 57 and 67 pp. Tetrahedral Al in the network of geopolymer is characterized by a narrow resonance at 57 pp. The other lines should be attributed to unreacted metakaolin. Simulation of the spectra enabled to quantify concentration of Al reflected in individual resonance. Curing in IR kiln seemed to improve only the degree of geopolymerization of M1000 samples, while mild mechanical mixing increased geopolymerization degrees in samples from both the metakaolins.

However the geopolymerization degrees by <sup>27</sup>Al MAS NMR spectra are little bit (< 5%) overestimated. Actually the resonance at 57 ppm reflect both Al (IV) in geopolymer and in some metakaolins.