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# Standardized Method in Testing Commercial Metakaolins for Geopolymer Formulations.

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## ABSTRACT

The majority of the technical and scientific information pertaining to commercial calcined kaolinitic clays of the type metakaolins (MK) are currently focusing on the pozzolanic reactivity and replacement of Portland cement. It is not adapted for geopolymerization and sometimes irrelevant. The aim of the present paper is to propose a customized test on metakaolins for geopolymer formulations. Standard commercialized Na and K silicate solutions with MR=1.7 were mixed with eleven commercial metakaolin samples (MK) and hardened at 80 °C. The temperature increase was recorded and the cumulative exothermal peak temperature is used to characterize very precisely the geopolymeric exothermicity of each commercial MK. In the Geopolymer standardized method, the geopolymeric exothermicity is expressed as the time in minutes it takes to reach the exothermal peak and its temperature, namely from the fastest to the slowest commercial MK: Metaver SF (21 min., 103 °C) - Argical M1200 (22 min., 103 °C) - PowerPozz White (26 min., 103 °C) - MetaMax (27 min., 103 °C) - MK Argeco (30 min., 93 °C) - Argical M1000 (34 min., 106 °C) - MK Pink (34 min., 106 °C) - Metaver I (45 min., 100 °C) - Metaver M (50 min., 93 °C) - Metaver N (>60 min., 82 °C) - MK 1300 (>60 min., 80 °C).

*Keywords:* standard, metakaolin, geopolymer, exothermicity, reactivity. © 2019 Institut Géopolymère. All rights reserved.

## 1. INTRODUCTION

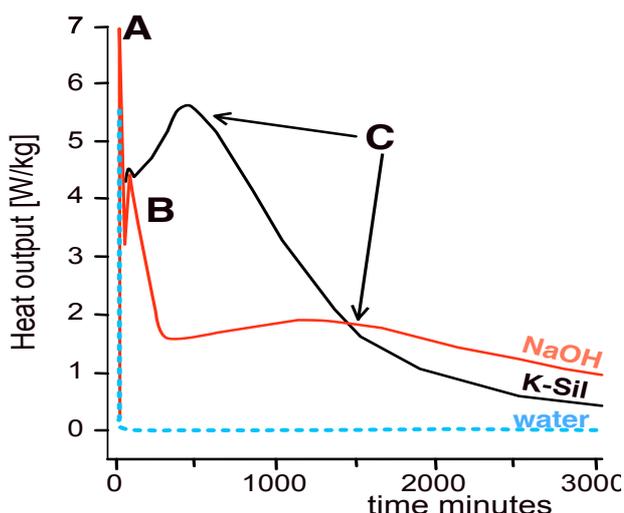
Geopolymers are inorganic polymers produced at low temperature, generally below 100°C. They consist of chains or networks of mineral molecules linked with covalent bonds. Their scientific and technological characteristics are described in the reference book *Geopolymer Chemistry and Applications* [1]. The present paper discusses some practical issues associated with metakaolin-based geopolymer and proposes a standardized method aimed at testing and selecting commercial metakaolins for cementitious and ceramic-like geopolymer formulations. Much of the pioneering research into geopolymers was conducted on calcined kaolinitic clays known under the generic term of

metakaolin (MK). In the past, the bulk of the commercialized MK or calcined clay was used essentially as fillers in the paper making and plastic industries. Its specific chemical reactivity towards alkalis remained confined to the production of very special products, namely synthetic zeolites, especially the type Zeolite A. Forty-three years ago, a new MK brand named *Argical*® supplied by the French company Argiles et Minéraux AGS, Clérac (now Imerys) had been manufactured with an advanced technology in a flash calciner instead of being roasted in a rotary kiln or a vertical multiple-hearth furnace (Herreshoff). A mixture of 1 kg Argical MK was mixed with 0.3 kg NaOH 12M solution and placed in a plastic bag for a while. After 1 hour, the temperature of the mix exceeded 100 °C. This test

demonstrated the powerful exothermicity and reactivity of this particular MK in alkaline medium. In addition, this flash-calcined MK also reacted very well with soluble (Na, K)-silicates and provided one of the basic ceramic-like geopolymer formulations [2].

### 1.1 Exothermic reactivity in isothermal conditions

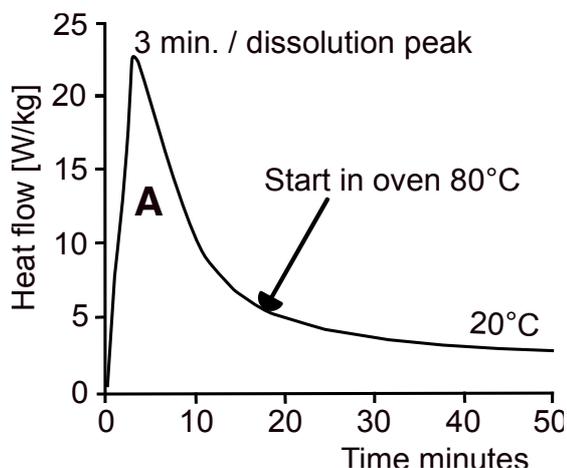
The distinctive exothermic property experienced at the beginning of the research on geopolymers was used in the Geopolymer Institute from the start to develop a standard method for quality control and selection of commercial metakaolins. It was successfully applied since then. This technique is now described in this paper. Despite this highly noticeable property, the amount of research carried out and the number of published papers on this topic is surprisingly low. The papers by Granizo and Blanco (1998)[3], Yao et al. (2009) [4], Kuenzel et al. (2013) [5] and Zhang et al. (2013) [6] are worth mentioning. They are essentially dealing with a better understanding of the geopolymerization kinetics and mechanisms involved in the transformation from metakaolin / alkali-silicates precursors to geopolymeric networks, under isothermal conditions in the temperature range 20–40°C. They used either Differential scanning calorimetry (DSC) or Isothermal conductive calorimetry (ICC).



**Figure 1:** Exothermicity, heat flow isothermal calorimetry at 20°C, DSC adapted from Yao et al. [4] with the systems NaOH/MK, K-Sil/MK and water/MK.

Under isothermal conditions at 20°C, three exothermic peaks (A, B, C) are observed in the calorimetric curve as shown in the Figure 1, with the systems NaOH/MK adapted from Yao et al. [4] who used the DSC method. In the case of the K-silicate/MK system (K-Sil in Figure 1), peak (B) would be absorbed by peak (C). The authors assigned the most intense peak (A) to the dissolution of metakaolin. It is sharp and appears immediately during mixing. They assigned the peak (B) to the polymerization of oligomers and peak (C) to the reorganization and stabilization of the geopolymer network. A control paste prepared by mixing water with MK under the same conditions provides the heat flow for peak (A) due to wetting and instant absorption of the solution on the surface of MK particles. It reaches 5.5 W/kg for pure water to be compared with 7 W/kg for the alkaline NaOH blend, i.e. a very small 1.5 W/kg heat flow difference.

According to the Figure 2, adapted from Zhang et al. [6] who studied the kinetics of geopolymerization of the NaOH/MK system by ICC method, the exothermal peak (A) is also very fast, measured at 3 minutes after mixing.

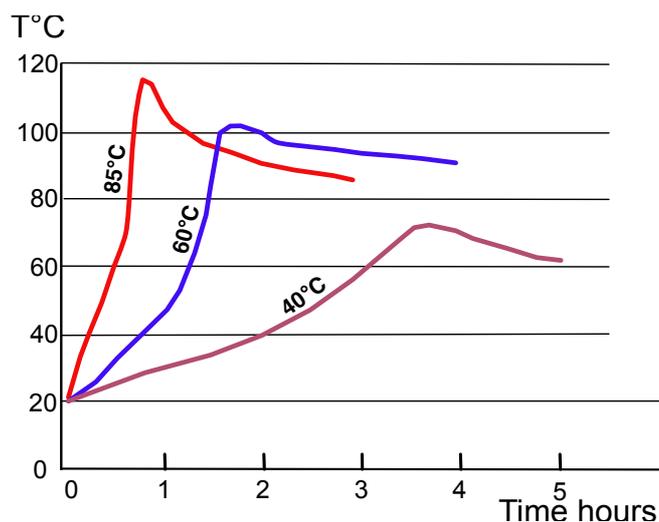


**Figure 2:** Exothermal peak (A) for NaOH/MK at 20°C, heat flow with time, after Zhang et al. [6]

### 1.2 Proposed standard with cumulative exothermal heat flow in non-isothermal conditions.

In the praxis, the mixing time allowed for the preparation of geopolymer batches is longer than the 2-3 minutes allocated for peak (A). In other words, this first part of exothermicity occurs in the mixing bowl, yielding a small increase of the mix temperature in the range of 1-3°C. Yet, in the present procedure that was developed for the practical selection of commercial metakaolins, the experimental method requests a mixing time of at least 10 minutes long, followed by the time allocated to the preparation of the sample and the coupling with the thermo-elements. The container is put in the oven after this lapse of time so that the recording of the temperature increase happens within 15-20 minutes after the start of the mixing, as displayed in Figure 2, with the mention, "Start in oven 80°C". Therefore, the sharp and fast exothermal peak (A) attributed to the wetting of MK cannot be assigned to the exothermic peaks measured in the present study (see Figure 3 adapted from Davidovits, 1988) [7].

The testing is run under non-isothermal conditions which generates a cumulative exothermal heat flow characterized by a sharp increase of the temperature in the sample. It was previously shown that the maximum temperature attained during geopolymerization depends on the curing temperature (Davidovits, 1988) [7]. As displayed in Figure 3, the exothermic peak for 85°C curing rose to 115 °C, after 45 minutes. With 60 °C curing, the exothermic peak developed 100 °C after one and half hour; with 40 °C curing temperature, the sample needed three and half hours for a peak at 70 °C. The speed and intensity of the exothermic polycondensation and setting time are therefore a function of the curing conditions. It also depends on the alkalinity of the soluble silicate hardeners, namely the higher the molar MR (Si/Alkali metal), the slower the setting time. The graphs of Figure 3 were obtained with MR=1.83.



**Figure 3:** Exothermic polycondensation of K-based geopolymeric binders for three different curing temperatures, 85°C, 60 °C and 40 °C curing temperatures, MR=1.83.

In the present study, the curing temperature was set at 80 °C. The alkali silicates had a MR=1.7 and the temperatures of the probes were recorded for 60 minutes. The financial investment for the device is very low, in the range of 60-80 euros.



**Figure 4:** Reactivity test, observing exothermicity, oven at 80 °C.

In Figure 4, the device is simultaneously recording the temperature of two probes. On the left is the tested probe, which is a mix of 60 g of MK with 100 g of K silicate or Na silicate. On the right is a blank probe, which is a mix of 60 g MK and 66 g water (same volume as in the tested probe) to check the rising of the temperature. The recorded data are transferred to a tabular sheet for further exploitation (graphics) and stopped after 60 minutes.

## 2. MATERIALS AND METHODS FOR STANDARDIZED TESTING

### 2.1 Commercialized metakaolins

Eleven different MK samples have been used to form geopolymers under identical processing conditions. The MK samples were *Argical M1200* and *M1000* (Imerys, France), *MetaMax* (BASF, Germany), *Powerpozz White* and *Metaver SF, I, M, N* (Newchem, Switzerland), *MK Argeco* (Argeco, France) and two MKs from China: *MK pink* and *MK 1300* used in a project run in Hong Kong. The chemical

composition (Table 1), LOI, mean particle size  $d_{50}$  are taken from the suppliers data sheets.

### 2.2 Calcination methods

The majority of the MK samples listed in Table 1 are calcined industrially in a rotary kiln and characterized by rounded massive aggregates of lamellar particles. The calcination cycle lasts 4 hours at 700–750°C with a production capacity of 10-12 tons / hour. The feed kaolinitic material is shaped as pellets which produce a temperature gradient in the pellet (Soleil-Raynaut, 2018) [8]. The resulting MK has to be milled after calcination. After dry grinding, the mean grain size  $d_{50}$  is in the range of 4 - 10  $\mu\text{m}$ . A lower grain size is achieved with wet grinding, as for *MetaMax* according to Mathur et al. (2001) [9].

**Table 1 :** Nine commercial MK samples data: content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in mass percentage (%) as oxides, LOI, mean diameter  $d_{50}$  and calcination methods. Data are from the suppliers.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	Other oxides	LOI	$d_{50}$ [ $\mu\text{m}$ ]	Calcination method
Argical M1200	54.4	39.4	4.2	1.0	1.5	Flash
Argical M1000	57.1	34.2	7.9	0.8	8-10.0	Rotary
Powerpozz	55.0	41.0	3.0	1.0	5.0	Herreshoff
MetaMax	52.5	43.8	3.2	0.5	1.4	Rotary +
Metaver SF	53.0	43.0	3.0	1.0	2.0	Flash
Metaver I	53.0	41.0	5.0	1.0	3.6	Rotary
Metaver M	53.0	42.0	4.0	1.0	4.0	Rotary
Metaver N	53.0	42.0	4.0	1.0	4.6	Rotary
MK Argeco	68.1	24.10	6.8	1.0	8.5	Flash
MK-pink	56.7	34.3	8.1	0.9	8-10.0	Rotary
MK-1300	60.0	34.2	5.0	0.8	10.0	Rotary

MK sample *PowerPozz* is calcined in a vertically oriented multiple hearth Herreshoff furnace. The material is moved by mechanical rakes across each hearth and then drops to the next hearth below. Each hearth has separate temperature controls and, unlike with rotary kilns, the time that the material is inside the furnace and the temperature gradient that the material is exposed to is precisely controlled ensuring the consistent production of high-purity highly reactive MK.

MK samples *Argical M1200*, *Metaver SF* are processed in a flash calciner with airflow at 950 °C for 1 second (production 1 tonne/h). Because the feed kaolinite is pre-milled before calcination, the mean grain size  $d_{50}$  is in the range of 1.5 -2  $\mu\text{m}$ . The feed for the sample *MK Argeco* is coarser, resulting in a higher  $d_{50}$  = 8.5  $\mu\text{m}$ .

### 2.3 Soluble alkali silicates

The industrialization and commercialization of MK-based geopolymer products result in reproducible and controlled

production processes of the liquid alkaline hardeners, Na silicate or K silicate. It also involves the implementation of a user-friendly manufacturing method for the preparation of a stable solution with long shelf life. Until recently, in order to reach the appropriate molar ratio MR,  $\text{SiO}_2:\text{Na}_2\text{O}$  or  $\text{SiO}_2:\text{K}_2\text{O}$ , the alkaline solutions have been prepared in the laboratory or in the production plant by mixing appropriate standard silicate solutions with NaOH or KOH. Others blend silica fumes with hydroxide solutions. A third method consists in mixing a silicate solution having a high molar ratio with another silicate possessing a lower molar ratio.

The chemical industry recently started the production of Na/K silicate solutions tailored to geopolymer applications. Because of changing safety regulations in the handling of caustic alkaline solutions, the lowest molar ratio MR  $\text{SiO}_2:\text{Me}_2\text{O}$  has been set at 1.7. The alkaline silicates chosen for the present study are:

- *GEOSIL 14517*, potassium silicate with a viscosity of 20 mPas at 20 °C and a MR = 1.7.
- *GEOSIL 34417*, sodium silicate with a viscosity of 350 mPas at 20 °C and a MR = 1.7.

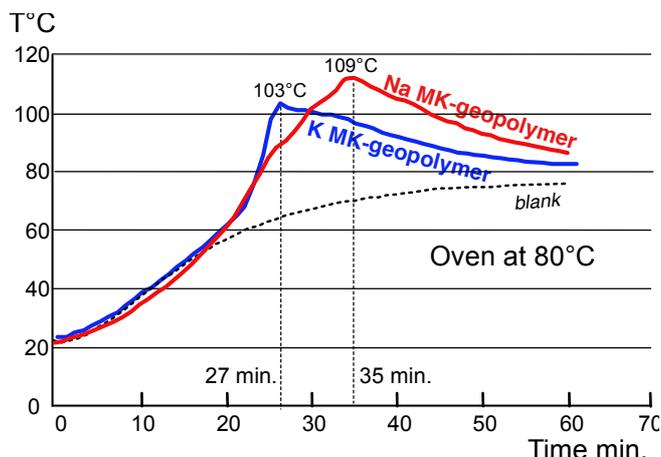
Manufactured by Woellner, Germany (Leute, 2018) [10].

#### 2.4 Thermography, cumulative exothermicity peak.

It plots the temperature of the sample during curing. The samples were prepared in the following way:

- Reactive mixture: 100 g of potassium silicate or sodium silicate solution were added to 60 g of MK and mixed in a planetary blender at 300 RPM for 10 minutes at 20°C.
- Hardening occurred in a plastic container covered by a lid or a film (but not hermetically sealed) and placed in an oven at 80°C, 15-20 minutes after starting mixing. The temperature was measured with electronic devices (thermoelements) or simple thermometers. Hardening samples must be covered in order to avoid any drying of the surface during the setting.

### 3. RESULTS.



**Figure 5:** cumulative exothermicity with MK *MetaMax*, K silicate and Na silicate solutions, MR=1.7.

#### 3.1 Na-based or K-based

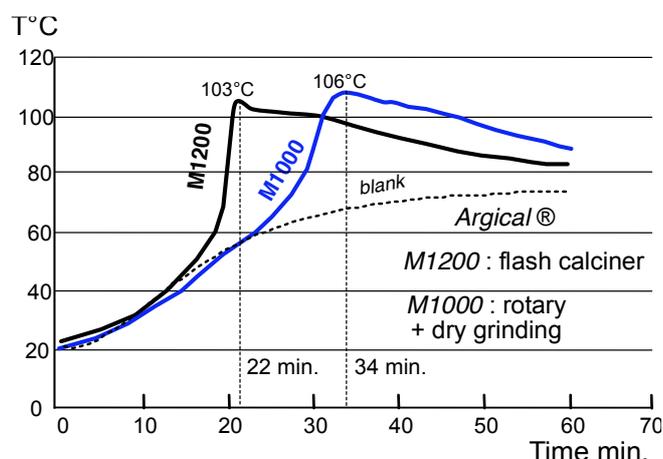
MK *MetaMax* was reacted with K silicate *GEOSIL 14517* (MR=1.7) and Na silicate *GEOSIL 34417* (MR=1.7) and

cured at 80°C. As shown in Figure 5, the K-based geopolymer reached 103°C at 27 minutes, 30% faster than Na-based geopolymer which developed a greater exothermicity with its peak at 109 °C but at 35 minutes.

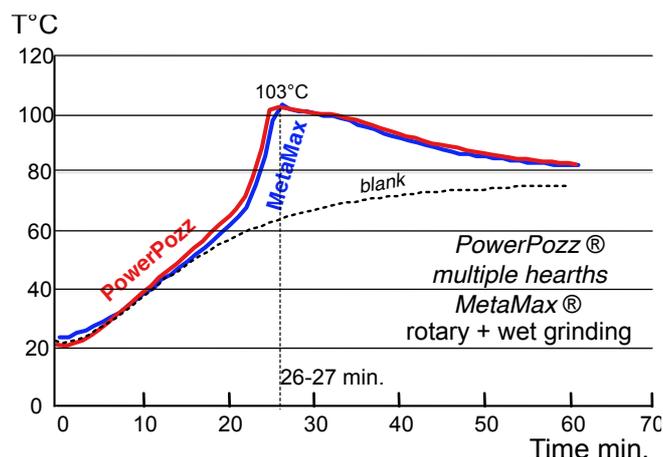
#### 3.2 Testing the commercial metakaolins

All other MK samples were tested with the K silicate formulation only, because it is easier to handle, due to its viscosity, lower than Na silicate (20 mPas for K instead of 350 mPas for Na).

For the two *Argical* brands (Figure 6) originating from the same geological source, Clerac, France, flash calcined *M1200* was the fastest, 22 minutes, compared with 34 minutes for rotary calcined *M1000*; yet, the exothermal peak for *M1000* was higher (106 °C) than for *M1200* (103 °C).

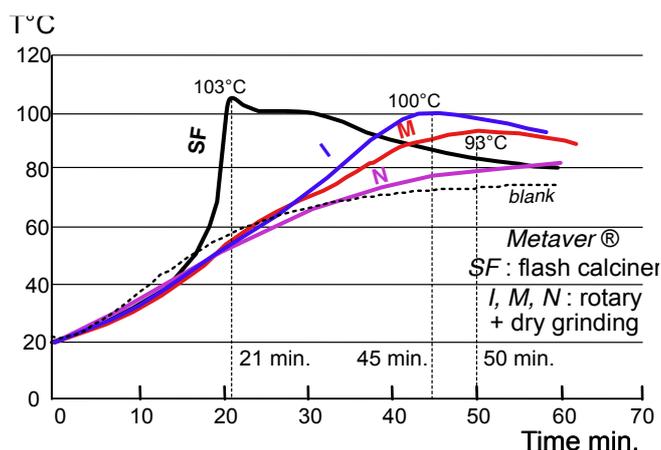


**Figure 6:** cumulative exothermicity for two MK samples *Argical M1200*, *M1000*, same geological sources (Clerac, France) and different calcining methods: flash and rotary.



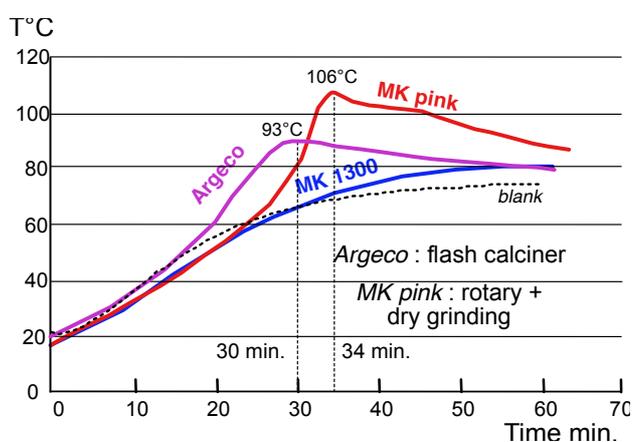
**Figure 7:** cumulative exothermicity for two MK samples *PowerPozz*, *MetaMax*, same geological sources (Georgia, USA), and different processing methods (multiple hearths and wet grinding).

The two MK samples manufactured in Georgia, USA, in the same geological formation, *PowerPozz* and *MetaMax* (Figure 7) had a practically identical thermograph: exothermal peak at 26-27 minutes and 103 °C. The manufacturing processes are different: Herreshoff system (multiple hearth) for *PowerPozz* vs. rotary calcination plus additional wet grinding for *MetaMax*.



**Figure 8:** cumulative exothermicity of four MK samples, *Metaver SF, I, M, N*: same supplier, different geological sources and calcining methods.

The four MK samples (*Metaver SF, I, M, N*) (Figure 8) supplied by NewChem, Switzerland, are originating from different (not defined) geological sources. The brand SF is flash calcined and gave a thermograph very similar to *Argical M1200*, 103 °C at 21 minutes. *Metaver I* (rotary calcined) was relatively slower than *Argical M1000* and develops 100 °C after 45 minutes. *Metaver M* was less reactive (peak at 50 minutes and 93 °C), whereas *Metaver N* was the slowest and did not produce any exothermal peak (82 °C at 60 minutes).



**Figure 9:** cumulative exothermicity for three MK samples, *MK pink, MK 1300, MK Argeco*, different geological sources and different calcining methods: flash and rotary.

According to the Chinese supplier, the two products *MK pink* and *MK 1300* are genuine metakaolins. *MK pink* (Figure 9) developed regular exothermicity, similar to *Argical M1000*, peak at 106 °C after 34 minutes. *MK 1300*, in contrast, did not produce any exothermal peak (80 °C at 60 minutes) and may not be named metakaolin. On the other hand, the flash calcined brand *MK Argeco* (Figure 9) behaved differently with a visible exothermicity at 30 minutes, 93 °C.

## 4. DISCUSSION

When in 1983, the Central Laboratory of the American cement company Lone Star Industries, Houston, USA,

started the development of the first metakaolin-based geopolymer cement [12], the cement PYRAMENT®, at least 10 different American MK brands had to be tested with the method described in this paper in order to find the right product which would react as a geopolymeric precursor in alkaline medium. For example, it was striking to discover that the MK sources for zeolite manufactures were according to Breck (1974) [13] of two types, one calcined at 550 °C (low temperature MK) and the second at 925 °C (high temperature MK). Both MKs reacted weakly and had been eliminated from the selection, among others.

Some years later, the flash calcined MK from Clérac, France, described in the Introduction, was no longer manufactured. It was replaced by another brand, also very popular in geopolymer research, *MetaStar 501* from ECC Int. UK, now Imerys. This was produced in a vertical multiple-hearth Herreshoff furnace and the kaolinitic clay extracted in Cornwall, UK. It became the reference material (coined Kandoxi and later MK-750) in all the research and applications carried out at the Geopolymer Institute and affiliated partners [14], until recently.

**Table 2:** Exothermic data for eleven commercial MKs: time in minutes at exothermic maximum, temperature at maximum measured during curing at 80°C, pozzolanic activity (data from suppliers) and calcination method.

	Time min. exo max	T°C max	Pozzolanic activity*	Calcination method
Metaver SF	21	103	1280*	Flash
Argical M1200	22	103	1370*	Flash
Powerpozz	26	103	rapid	Herreshoff
MetaMax	27	103	-	Rotary +
MK Argeco	30	93	-	Flash
Argical M1000	34	106	1150*	Rotary
MK Pink	34	106	-	Rotary
Metaver I	45	100	rapid	Rotary
Metaver M	50	93	very rapid	Rotary
Metaver N	>60	82	rapid	Rotary
MK 1300	>60	80	-	Rotary

\* Chapelle test.

In Table 2, the commercial MK samples are listed starting from the fastest, *Metaver SF*, to the slowest (not hardening) formulation *MK 1300*. Flash-calcined *Metaver SF* and *Argical M1200* reached the fastest exothermal peak at 21-22 minutes, confirming previous studies carried on different MK samples. The exothermal peak is strongly dependent on the calcination method.

According to Kuenzel et al. (2013) [5], even at ambient temperature (22 °C), the geopolymer paste made using *Argical M1200* set rapidly, with final set after 15 hours. This was surprising for the authors because their studies clearly showed that *Argical M1200* contains a lower content of

reactive Si and Al and lower Al (V) amount, when compared with *MetaMax*. The longest setting time (42 hours) was for the geopolymer made using *MetaMax* which contained the highest Al (V) content at 86% compared with 70% for *Argical M1200*. It should have been the reverse, according to some theories on reactivity. In the present method, *MetaMax* reached its exothermal peak at 27 minutes, 103 °C, and was 22% slower than *Argical M1200* (22 minutes and 103 °C).

In Table 2, the pozzolanic activity values measured with the modified Chapelle test towards Ca(OH)<sub>2</sub>, are data obtained from the suppliers, targeted to Portland cement replacement. The test consists of reacting, for 16 hours at 90 °C., 1 g of metakaolin with 2 g of CaO in the presence of 250 ml of water. The non-combined lime is then analyzed and the result is expressed in mg of Ca(OH)<sub>2</sub> fixed per gram of metakaolin. The values provided by some suppliers are namely : 1370 mg for *Argical M1200*, 1280 mg for *Metaver SF* and 1150 mg for *Argical M1000*. The values obtained with the Chapelle test seem to correlate the exothermal data measured here for these three MKs. Flash-calcined MKs are reacting faster than those calcined in a rotary kiln. But the Chapelle test and any equivalent pozzolanic activity measurement are more complicated to run (16 hours at 90°C under reflux conditions and additional chemical analysis of the reacted Ca(OH)<sub>2</sub>) than the present geopolymeric exothermicity : 1 hour at 80°C and a simple thermoelement device.

The two Chinese products, *MK pink* and *MK 1300*, were sold in Hong Kong and labeled "metakaolin". The present method showed a clear cut difference between the two: *MK pink* developed an exothermal peak at 34 minutes, 106 °C, (Table 2) similar to the well-referenced French *Argical M1000* (34 min., 106 °C), whereas *MK 1300* had practically the same temperature history as the blank probe. *MK pink* is a good product for geopolymer formulations compared with *MK 1300* which does not set.

Among the 11 MK samples studied, two did not produce detectable exothermicity after 60 minutes at 80 °C: *Metaver N* (Fig. 8) and *MK 1300* (Fig. 9). These two brands are sold as pozzolanic admixtures to Portland cement. According to the supplier, *Metaver N* has a reactivity towards lime Ca(OH)<sub>2</sub> qualified as "rapid" (Table 2, Pozzolanic activity), in other words, identical to the other brand *PowerPozz* marketed by the same supplier. But in the present exothermal test, run at 80 °C, *MK PowerPozz* has an exothermal peak at 26 minutes and 103 °C, whereas *Metaver N* has none. *PowerPozz* is an excellent MK product for geopolymer formulations compared with *Metaver N* which does not set after 60 minutes. It is therefore obvious that the simple pozzolanic reactivity measured for Portland cement admixtures does not provide any valuable information for its use as a component in geopolymer formulations.

The product *MK Argeco* was specially developed for the pozzolanic replacement of Portland cement. It was also tested for the manufacture of geopolymer concrete, building elements and masonry units (Pouhet and Cyr, 2016) [11]. The starting raw material is an iron-containing kaolinitic clay. The resulting MK contains 65% by mass of quartz, 48-49%

metakaolinite and 4-5% Fe<sub>2</sub>O<sub>3</sub>. It is flash calcined and reacts faster (30 min., 93 °C) than similar MK samples produced with a rotary kiln. But because of the high amount of quartz, the exothermic effect becomes diluted and lower at 93 °C compared with *Argical M1000* (34 min., 106 °C) and *MK pink* (34 min., 106 °C) (Table 2).

#### 4.1 The addition of metakaolin in Portland cement

Before the mid 1990s, MK was a niche product and its manufacturing capacity was relatively small. Then, the Portland Cement industry discovered the beneficial properties of calcined kaolinitic clays, and at the end of the 2000s, MK manufacture became a global industry with the emergence of the so-called high-reactivity-MKs HRM made from good quality white kaolinitic clay sources, on the one hand, and on the other hand, lower grade iron containing calcined kaolinitic clays. The clay-processing industry concentrated its investments in the manufacture of the high-volume products tailored for blending with Portland cement. As a consequence, products like *MetaStar 501* produced in the UK progressively became no longer attractive. In 2010, its production was stopped and Imerys went back to the Clerac site, reopening the small flash-calcining facility and, at the same time, increasing the production capacity of its rotary kilns. The Cornwall *MetaStar 501* was replaced by Clerac *Argical M1200* (flash calcined) and *Argical M1000*, roasted in the rotary kilns. A new *MetaStar 501* manufactured in Georgia, USA, was tested in the present study. However, its physicochemical properties do not correspond to the original MK produced in Cornwall and referenced in the geopolymer literature (Kuenzel et al., 2013) [5]. It was therefore decided to refrain from presenting the results, to avoid any confusion between the data obtained with the old product - which was the reference MK for more than 30 years - and the new.

MK-based geopolymers have been successfully introduced in various markets including paints, grouts, and ceramic-like products. But presently, their successful commercialization remains strongly dependent on the availability of industrially manufactured MK products tailored to geopolymer ceramic-like applications. Yet, this requires the usage of reproducible and easy to work methods for daily quality control. The aim of the present paper was to provide a response to this demand and to propose a technique adapted for geopolymerization.

#### 4.2 Present situation

As a matter of fact, the majority of the technical and scientific information pertaining to commercial MK currently focuses on their application as Portland cement additives (pozzolans). They provide data on pozzolanic reactivity towards Ca(OH)<sub>2</sub>, like the Chapelle test which is applied to predict the ability of MK to replace a certain amount of Portland cement, generally not higher than 20% by mass. But in any ceramic-like geopolymer formulation, the role devoted to MK is fundamentally different. Geopolymerization steps do not follow the mechanisms of pozzolanic and hydration activities.

Notwithstanding the fact that the industry was reorganizing its production to meet the increasing demand as a

replacement product for Portland cement, or because of it, geopolymer scientists continued to calcine their own MK in their labs. For the purpose of understanding the relationship between raw kaolinitic clay source, reactivity and exothermicity, the Geopolymer Institute had set standard parameters which could replicate the industrial processing of *MetaStar 501*. They involved the grinding of the clay and calcining in an electric oven, in air, at 750 °C for 3 hours [hence the name MK-750]; the heating time from 20 °C up to 750 °C was 1h 30 min., the cooling time 1h 30 min, totalizing 6 hours in the furnace [14]. But in the literature, the manufacturing conditions vary dramatically, so that it is hard to compare any results deriving from this research.

The following non-exhaustive list is representative of the situation; it gives the calcination temperature and the time; however, it does not mention whether it includes the heating and cooling times: - Zibouche *et al.*, (2009) [15]: 800 °C, 2 h. - Zhang Yunshen *et al.*, (2009) [16]: 700 °C, 12 h. - Rowles *et al.*, (2009)[17], 750 °C: 24 h. - Yao *et al.*, (2009)[ 4], 900°C: 6 h. - Medri *et al.* (2011) [18], 750 °C: 15 h. Others started using commercial brands: - Zhang *et al.*, (2009) [16], *MetaMax* from Engelhardt (now BASF). - Favier *et al.*, (2013) [19], *Argical M1000* from Imerys. - Medri *et al.*, (2010) [20], *Argical M1000* and *M1200 S* from Imerys.

As for the soluble (Na, K) silicates, it was only recently (2015) that the chemical industry developed and began to commercialize soluble silicates specially tailored for ceramic-like geopolymer applications. The present study was performed exclusively with these products. Because alkaline hardeners are more or less caustic depending on their concentration in Na<sup>+</sup> or K<sup>+</sup> cations, the Geopolymer Institute introduced in 2008 the notion of *user-friendly* geopolymeric precursors. The lower value for the molar ratios SiO<sub>2</sub>:Na<sub>2</sub>O or SiO<sub>2</sub>:K<sub>2</sub>O, was set at 1.45. Today, because of the European REACH directives and safety regulations, the industry sets this value at 1.70 for Na silicates and K silicates.

## 5. CONCLUSION: creating a Geopolymer Institute Standard for metakaolin characterization.

Contrary to the alkali silicate industry, the MK manufacturing business does not test nor recommend any MK for geopolymer applications so far. It is essentially focused towards Portland cement replacement or admixture and relying on data to measure the pozzolanic activity towards Ca(OH)<sub>2</sub>. The aim of the present paper was to provide a technique based on the exothermal exothermicity of MK with alkali silicates. The technique which was introduced 35 years ago, was mentioned in the reference book on geopolymer chemistry (Davidovits 2008-2015) [1]) and only recently standardized in our laboratory for the study of eleven commercialized metakaolin brands.

Why choose the 80 °C curing temperature instead of 60 °C or 40 °C like in Fig. 3 ? Because what is important for the scientist in the laboratory, or the technician in the plant, is to know how fast a product will set and what temperature it will reach inside the hardening ceramic, in order to select the

right equipment, the appropriate material for the mold, etc. The method is very simple, requires low investment and can be run at any time either in a sophisticated laboratory or in a simple production plant. It provides an immediate answer, within minutes, to the question raised before testing or purchasing any products which are sold under the label "metakaolin", namely: is it adapted to geopolymer formulations?

The MK industry lists pozzolanic activity in their materials data sheets for Portland cement applications. A good step towards standardization would be to include the Geopolymer Institute method which measures the geopolymeric exothermicity developed at 80°C, namely the time in minutes to reach the exothermal peak and the maximum temperature:

- *Metaver SF* (21 min., 103 °C)
- *Argical M1200* (22 min., 103 °C)
- *PowerPozz White* (26 min., 103 °C)
- *MetaMax* (27 min., 103 °C)
- *MK Argeco* (30 min., 93 °C)
- *Argical M1000* (34 min., 106 °C)
- *MK Pink* (34 min., 106°C)
- *Metaver I* (45 min., 100 °C)
- *Metaver M* (50 min., 93 °C)
- *Metaver N* (60 min., 82 °C)
- *MK 1300* (60 min., 80 °C).

## REFERENCES

- [1] J. Davidovits, *Geopolymer Chemistry and Applications*, 2nd ed. 2008, 3rd ed. 2011, 4th ed. 2015, Geopolymer Institute, ISBN 4th ed. 9782951482098.
- [2] J. Davidovits, *Polymère Minéral*, French Patent Applications FR 79.22041 (FR 2,464,227) (1979) and FR 80.18970 (FR 2,489,290) (1980); US Patent 4,349,386, (1982) Mineral polymers and methods of making them.
- [3] M.L. Granizo, M.T. Blanco-Varela, A. Palomo, Influence of the starting kaolin on alkali-activated materials based on metakaolin. Study of the reaction parameters by isothermal conduction calorimetry, *J. Mater. Sci.* 35 (2000) 6309–6315.
- [4] X. Yao, Z. Zhang, H. Zhu, Y. Chen, Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry, *Thermochimica Acta* 493 (2009) 49–54.
- [5] C. Kuenzel, T.P. Neville, S. Donatello, L. Vandeperre, A.R. Boccaccini, C.R. Cheeseman, Influence of MK characteristics on the mechanical properties of geopolymers, *Applied Clay Science* 83–84 (2013) 308–314.
- [6] Zhang, Z., Provis, J.L., Wang, H., Bullen, F., Reid, A., Quantitative kinetic and structural analysis of geopolymers. Part 2. Thermodynamics of sodium silicate activation of metakaolin, *Thermochimica Acta* 565 (2013) 163–171.
- [7] J. Davidovits, *Geopolymer Chemistry and Properties*, Geopolymer '88 Conference, Proceedings (1988) 25–48.
- [8] V. Soleil-Raynaut, The manufacture of metakaolin, Geopolymer Camp 2018, web: <https://geopolymer.org/fichiers/?dir=gpcamp-2018> (accessed September 29, 2018).
- [9] S. Mathur, K.A. Gruber, H.J. Reid, Manufacture of Improved Metakaolin by Grinding and Use in Cement-

- Based Composites and Alkali-Activated Systems, US Patent 6,221,148 (2001).
- [10] M. Leute, Geosil – ready to use alkaline activator solutions for Geopolymers, Geopolymer Camp 2018, web: <https://geopolymer.org/fichiers/?dir=gpcamp-2018> (accessed September 29, 2018).
- [11] R. Pouhet, L. Cyr, Formulation and performance of flash metakaolin geopolymer concretes, *Construction and Building Materials* 120 (2016) 150–160.
- [12] J. Davidovits, J.L. Sawyer, Early high-strength mineral polymer, US Patent 4,509,985, (1985), filed February 22, 1984.
- [13] D.W. Breck, Zeolite Molecular Sieves, Structure, Chemistry and Use, John Wiley & Sons, New York, 771 pp. (1974).
- [14] J. Davidovits, Geopolymers: Ceramic-Like Inorganic Polymers, *J. Ceram. Sci. Technol.* (2017) 1-16.
- [15] F. Zibouche, H. Kerdjoudj, J.B. d'Espinose de Lacaillerie, H. Van Damme, Geopolymers from Algerian metakaolin. Influence of secondary minerals, *Applied Clay Science* 43 (2009) 453–458.
- [16] Y. Zhang, Y. Jia, W. Sun, Z. Li, Study of ion cluster reorientation process of geopolymerisation reaction using semi-empirical AM1 calculations, *Cement and Concrete Research* 39 (2009) 1174–1179.
- [17] M.R. Rowles, B.H. O'Connor, Chemical and Structural Microanalysis of Aluminosilicate Geopolymers Synthesized by Sodium Silicate Activation of Metakaolinite, *J. Am. Ceram. Soc.* 92 [10] (2009) 2354–2361.
- [18] V. Medri, S. Fabbri, A. Ruffini, J. Dedecek, A. Vaccari, SiC-based refractory paints prepared with alkali aluminosilicate binders, *Journal of the European Ceramic Society* 31 (2011) 2155–2165.
- [19] A. Favier, G. Habert, J.B. d'Espinose de Lacaillerie, N. Roussel, Mechanical properties and compositional heterogeneities of fresh geopolymer pastes, *Cement and Concrete Res.* (2013) 48 9–16.
- [20] V. Medri, S. Fabbri, Dedecek, Z. Sobalik, Z. Tvaruzkova, A. Vaccari, Role of the morphology and the dehydroxylation of metakaolins on geopolymerization, *Applied Clay Science* 50 (2010) 538–545.