UNIVERSITÀ DEGLI STUDI DI PADOVA

PHD COURSE IN INDUSTRIAL ENGINEERING

CURRICULA MATERIALS ENGINEERING

FINAL DISSERTATION

XXXI CYCLE

DEVELOPMENT OF BRAKE COMPONENTS:
GEOPOLYMER BASED BRAKE PADS

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The important thing is not to stop questioning.
Curiosity has its own reason for existence.
One cannot help but be in awe when he contemplates
the mysteries of eternity, of life, of the marvelous structure of reality.
It is enough if one tries merely to comprehend a little of this mystery each day.

La cosa importante è non smettere mai di domandare.
La curiosità ha il suo motivo di esistere.
Non si può fare altro che restare stupiti quando si contemplano
i misteri dell'eternità, della vita, della struttura meravigliosa della realtà.
È sufficiente se si cerca di comprendere soltanto un poco di questo mistero tutti i giorni.
Non perdere mai una sacra curiosità.

(Albert Einstein)

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Zio Luigi, sei scomparso 3 anni fa, proprio quando stavo per iniziare il dottorato. Questa tesi è dedicata a te.

ABSTRACT

The brake disc technology is the most used on commercial vehicle. The main focus of this project was the substitution of the phenolic resin, which is normally used as matrix in brake pads, with inorganic matrix, and in particular with geopolymer.

The inspiration comes from their inorganic structure. Geopolymers have better thermal properties than organic resins, which typically decompose by oxidation starting from ~400°C. In fact, during the braking events temperature in the order of 600°C-800°C can be reached. The research has been financed by ITT Italia s.r.l a world company leader on the production of brake pads. On the base of the guidelines of the company, the goal of the project has been the substitution of the phenolic resin with the geopolymer matrix and without any modification on the production process of brake pads.

Brake pads were produced using a warm press technology in dry conditions. During the pressing step occurs the phenolic resin's crosslinking which could be completed through a post-curing in oven.

Based on the fact which the geopolymer are synthesized in solution, the first part of the project was focused on the development of geopolymer matrices suitable to be processed in the same conditions used to produce phenolic resin-based brake pads.

Two geopolymer system have been developed:

1. the hydrothermal dry synthesis of hydrosodalite from the reaction of kaolin and sodium hydroxide;
2. the cold sintering of geopolymer powder based on metakaolin and sodium silicate.

The best pressing conditions for the two system were evaluated on the base of their effect on mechanical properties and physical proprieties of geopolymer matrix. To evaluate the feasibility of the production in large scale of the geopolymer based brake pads, for the geopolymer matrices two goals have been followed at the same time:

1. The scale up at an industrial level for the geopolymer matrix production. Tests were carried out before at lab scale and subsequently with industrial technologies.
2. The optimization of the brake formulations has been done in ITT Italia s.r.l. on the base of physical properties and friction characterization of geopolymer based brake pads.

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INTRODUCTION

Since 1980s, it was public knowledge that asbestos is a carcinogen material. However, in Europe, USA and Australia asbestos have been totally banned for new applications only from 2005. Asbestos is cheap and provided friction linings with excellent durability and thermal resilience, and for this reason asbestos fibers have been used as reinforcing material in brake pads since 1900s. [1][2]

The future of brake pads is green, in fact similarly to asbestos in Europe, and in particular in USA for copper is happening something similar. In California the legislation requires that by 1 January 2025, brake manufacturers/importers selling in California must self-certify that their pads contain no more than 0.5 percent by weight of copper. [3]

These regulations and limits are related to the debris generated from friction materials during the braking events.

State-of-the-art friction materials for brake pads are constituted by composite materials, specifically formulated to ensure proper friction and wear performances under the sliding contact conditions of braking events. The most diffused type of matrix for brake pads is the phenolic resin. It is an organic resin suitable for the manufacturing of brake pads, because it is a low-cost thermosetting resin which cross-link in situ during the production of brake pads with a hot-molding step. A post-curing could be done to complete the hardening of the resin. During the production of brake pads, volatile organic compounds as formaldehyde could be released, and during the braking events, high-temperature organic-based hazardous derivatives are generated. In fact, during the braking events temperature in the order of 600°C-800°C can be reached. Moreover, the degradation of the organic matrix causes the fade and so the loss in friction properties. [2]

Similarly to asbestos and copper, recent studies investigate the exhausted and non-exhausted motor vehicle emissions. Brake wear has been recognized as one of the most important non-exhaust traffic-related source. Nation as France, Germany are developing a new european legislation to decrease the emissions associate to brake system. On average, 18% of the airborne PM was carbonaceous material, and with the non-exhausted gas are related to the degradation of the phenolic resin. [4]

The inspiration, for the use of a geopolymer matrix in brake system and in brake pads, comes from their inorganic structure. It's known that geopolymers possess better thermal properties than organic resins, which typically decompose by oxidation starting from ~400°C [5]. The research has been financed by ITT Italia s.r.l a world company leader on the production of brake pads. On the base of the guidelines of the company, the main goal of the project has been the substitution of the phenolic resin with the inorganic matrix and without any modification on the production process of brake pads.

The innovative approach of the project was related to the use of geopolymers as matrix in their original form, and without any modifications as pyrolysis and ceramization. In fact, other inorganic materials as commercial preceramic polymers have been yet investigated as matrix of pyrolyzed brake pads [6], while geopolymer have been used as filler [7].

Geopolymer were the more interesting candidate for the project, in relation with their low cost and with the possibility to tune the properties of the geopolymer as a function of the applications.

THESIS ORGANIZATION

The state-of-the-art of brake pads and geopolymers will be presented in the Background, with focus for brake pads on the technology, materials and friction/wear consideration. For geopolymers definitions, reaction mechanism and application will be described.

Chapter 1 describes materials and method used for the production and characterization of geopolymer components and geopolymer based brake pads.

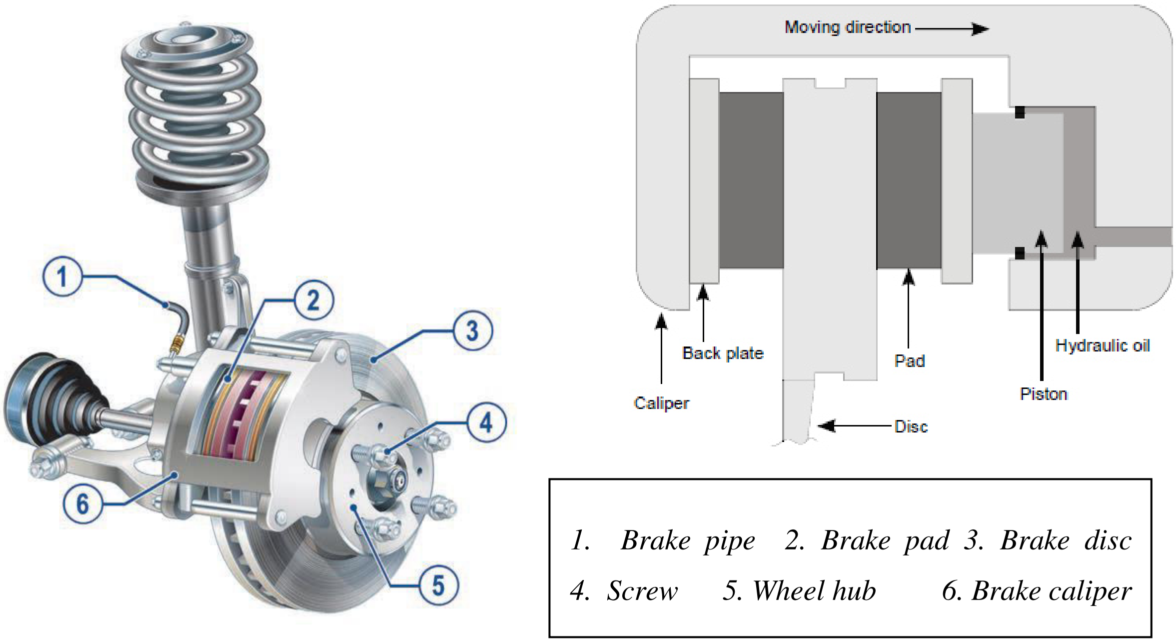
Chapter 2 reports on the use of a kaolin-sodium hydroxide as geopolymer matrix for brake pads. Contrary to phenolic resin binders for this geopolymer system, the matrix based on sodalite is obtained during the hot molding process for the production of pads, thanks to a hydrothermal reaction which happens in absence of water. The reaction mechanism has been studied and the stoichiometric of the system has been optimized. Brake pads based on this matrix have been developed but the limits related to the use of kaolin-sodium hydroxide system will be shown.

Chapter 3 present the best geopolymer system developed during the project. The system is based on the cold sintering of geopolymer powder. Using a DOE approach, the effect of the geopolymer composition and powder properties have been studied to enhance the sintering of the powder. Brake pads with promising properties have been developed for this geopolymer system.

BACKGROUND

I. Brake disc technology

The aim of a brake systems is to convert the vehicle's kinetic energy into heat energy, to decelerate or to stop a vehicle. The brake disc technology is the most diffused braking system on modern light and commercial vehicle, **fig. I.I.**



1. Brake pipe 2. Brake pad 3. Brake disc
4. Screw 5. Wheel hub 6. Brake caliper

Figure I.I: Typical brake disc system structure [8][9]

The main components which constitute the disc brake system are: the disc, the caliper and the two pads. The working of a disc-brake assembly is based on a movement on the brake pedal, which forces a piston to move in the master cylinder: this causes a pressure on the liquid ahead of the piston, forcing the liquid under pressure against the caliper. As a consequence, the pistons in the caliper forced the pads against the disc.

The brake disc and the brake pads are the most important parts of the braking system.

It's important that the major part, ideally more than the 80%, of the heat generated by friction has to be removed from by the disc, which could possess particular geometry able to eliminate in an appropriate way the heat. Ventilated discs are the typical example.

Grey cast iron with a perlitic matrix is the widely used material for brake discs. The benefits of using it as material are: good castability and machinability, high thermal conductivity, resistance to brake fade and low cost. Aluminum and CMCs are other materials used for disc.

Aluminum based discs possess good wear and corrosion resistance, high thermal conductivity and a lower density which permits to decrease the weight, but the maximum working temperature is lower than grey cast iron. Silicon carbide-based brake discs reinforced with carbon fibers, are used in high performance vehicle thank to superior mechanical and fade properties, however the price is very high compared to grey cast iron and aluminum. [2][8][9]

II. Brake pads

In order to have an appropriate behavior, brake pads must:

a) Maintain a sufficiently high friction coefficient with the brake disc;
b) Not decompose or break down in such a way that the friction coefficient with the brake disc is compromised, at high temperatures;
c) Exhibits a stable and consistent friction coefficient with the brake disc.
d) Have a dumping behavior to give a comfort during the braking and to prevent noise and vibration

To guarantee the listed requirements a brake pads is structured of different parts as shown in **fig. I.II**.

1-Friction material
2-Underlayer
3-Adhesive
4-Backplate
5-Shim
6-Chamfer
7-Slot

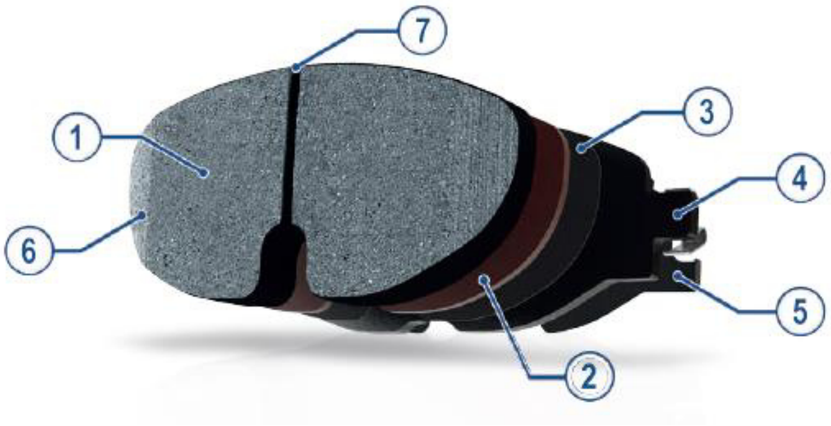


Figure I.II: Brake pad structure [8]

The back plate permits to distributed homogeneously the force from piston. The underlayer gives damping properties to the pad and permits to insulate the friction material from the back plate to inhibit the heating of the caliper; underlayer it's a phenolic resin-based composite, to have a good coupling with the friction material. Shim, chamfer and slot helps to reduce the squeal noise, to allow the bending and to help the elimination of friction dust.

The most important part is the friction materials, which is directly in contact with disc. A commercial friction material contains more than 20 components to have the desired properties. The friction coefficient has to be stable considering different velocities in the range of 0.3-0.5 so an appropriate mix of the different ingredients has to be developed in function of the vehicle and the desired properties. The different ingredients can be classified into five classes:

Binder: it is the material which holds all the components together. As described in the introduction, phenolic resins are usually used as binders. In function of the resin properties and composition different wear resistance could be observed [11]. Other types are silicone-modified and epoxy-modified resins. For the project the development of a geopolymer binder has been the goal of the research.

Reinforcements: Asbestos have been for years the most used fibers in friction formulation. Fibers permits to increase toughness and flexural resistance of friction material. Ceramic and glass fibers have a good thermal resilience and stiffness, but they are brittle. Metallic fibers as steel, copper and brass are also used because they permit to increase the thermal conductivity and to remove the heat from the friction surface. Steel fibers in particular are subjected to corrosion and they have a significant effect on the disc wear. On the development of friction material for the project, and with the focus to have a "green" friction formulation, copper-based fibers have not been considered.

Abrasives: The role of abrasive is to increase the friction coefficient. They have to be hard enough (7-8 Mohs hardness) to abrade the brake disc, and they removed the iron oxide from the gray cast iron disc surface. However high amount of abrasives causes an increasing in disc wear rate. Metal oxide and silicate are the commonly used abrasive: zirconium oxide, aluminum oxide, chromium oxide and zirconium silicate. Silicon carbide is also used but in lower amount due to the high cost.

Lubricants: For brake pads solid lubricants are used. The lubricants contrast the effect of abrasive, to decrease and to stabilize the friction coefficient. Graphites and metal sulphides are the most used lubricants material, thanks to their layered structure.

Fillers: it's a general term which describe materials used to decrease the cost of the brake pads, but in general in this class have to be considered all the material that permits to have one or more effects on the brake pads properties, not described in the other classes. Calcium carbonate and barium sulphate improve the heat stability. Calcium carbonate permits also to decrease the cost and the barium sulfate behave as a weak abrasive. Mica and vermiculite help to reduce the braking noise. Rubber is used both in the friction materials and in the underlayer to reduce noise and to improve the dumping materials, thanks to its viscoelastic properties. [2][8][9][10]

A common classification based on the metallic content of friction materials, it's used to distinguish the types of brake pads:

- Semi-metallic : %(Fe + Cu) ≥ 50%wt
- Low steel: %(Fe + Cu) = 10 – 50% wt
- Non-asbestos organic (NAO) : %(Fe + Cu) < 10%wt

III. Wear mechanism in pad-disc interface

> *Consider a vehicle with a total weight of 2000 [kg] moving at a speed of 100 [km/h] which is fitted with four disc brake systems. Assume that it is braked and stopped in 5 [s]. By ignoring smaller contributions, e.g. rotational kinetic energy of different parts, kinetic energy of the vehicle, expressed as* $\frac{1}{2}mv^2$*, is 771.6 [kJ]. So by assuming that all of this energy is converted to heat, average dissipation rate is 154.3 [kW]. As the brakes mounted on front axle approximately have 60-80% of a vehicles braking power, so each front brake might be dissipating about 60 [kW] on average. But this power is not uniformly distributed over the pad surface as real contact area is approximately 20% of the apparent contact area. This could be compared to the engine power of about 110-140 [kW] available in a vehicle with a 2.4 liter gasoline engine.*
>
> *Asim Rashid , Overview of Disc Brakes and Related Phenomena - a review*

The tribology of a friction material is complex system, because the brake pads is a composite material with a lot of constituents. As described only a part of the pad works during the brake event, so the wear is related to the interaction of disc and pad surfaces, considering the different material which interact during the braking.

Friction can be described as resistance to the relative sliding motion of bodies in contact. The presence of asperities on the surfaces causes some contact spot, and the sum of the spot constitutes the real area of contact. Considering the interface between pad and disc we have a dry friction system. Different friction mechanisms occur during braking: adhesion, elastic and plastic deformation of asperities, ratcheting, fracture of asperities and third body mechanism. These phenomena are also related to the wear of the interface. [9][12][13]

Considering for the disc a relative sliding velocity v_t in the direction t, and Fn the normal force between disc and pads, the friction force (perpendicular to the normal force) is:

$$F_r = \mu F \ , \tag{I.I}$$

where μ is the coefficient of friction (CoF). Before the sliding motion it is called static CoF (μ_s) and during motion it is called kinetic CoF (μ_k). In general μ_s is higher than μ_k. [14] In general friction increases with an increase of real area of contact, and the real area is almost linearly proportional to the load [13].

Considering the wear of the pad or disc we can use the simple Archard's wear law [15]:

$$\Delta W = kFs \ \ , \tag{I.II}$$

where ΔW is the worn volume, k the coefficient of wear and s the sliding distance. It is a simplified way to describe the wear, but it is enough for our objectives.

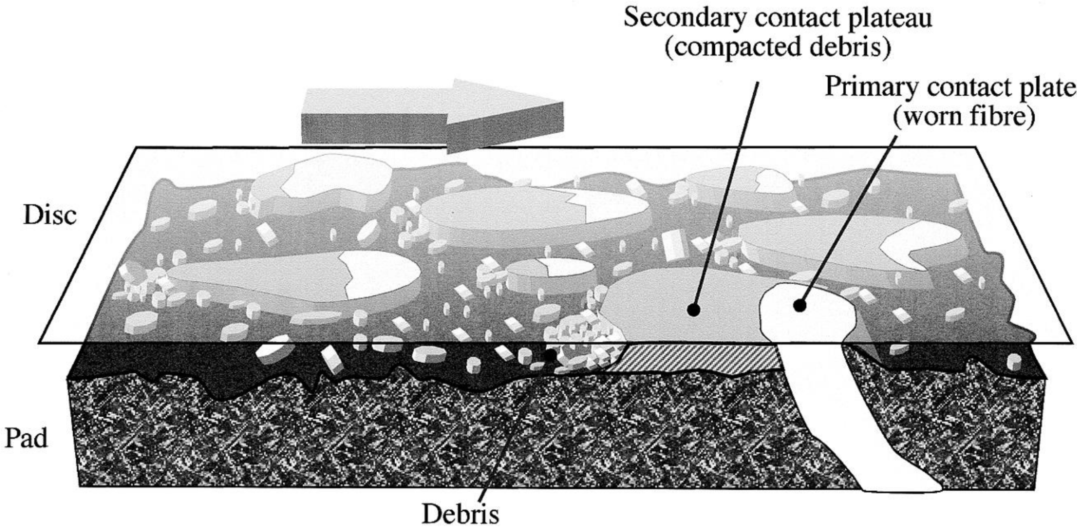


Figure I.III: Mechanism of interface disc/pad based on contact plateau [16]

Similar to friction different mechanism can be found for wear: adhesion, abrasion, fatigue, corrosion, chemical wear etc. Due to different wear mechanisms, particles of varying sizes detach from pad and disc surfaces which are crushed and milled down to smaller particles while they are trapped between the contact surfaces. The mixing of particles and their oxide form the third body. Part of the third body remains between disc and pad; the excess is released from the system.

Two approaches/mechanisms are used to study the phenomena which occurs at the disc/pad interface: formation of contact plateau and effect of the third body layers formed between pad and disc.

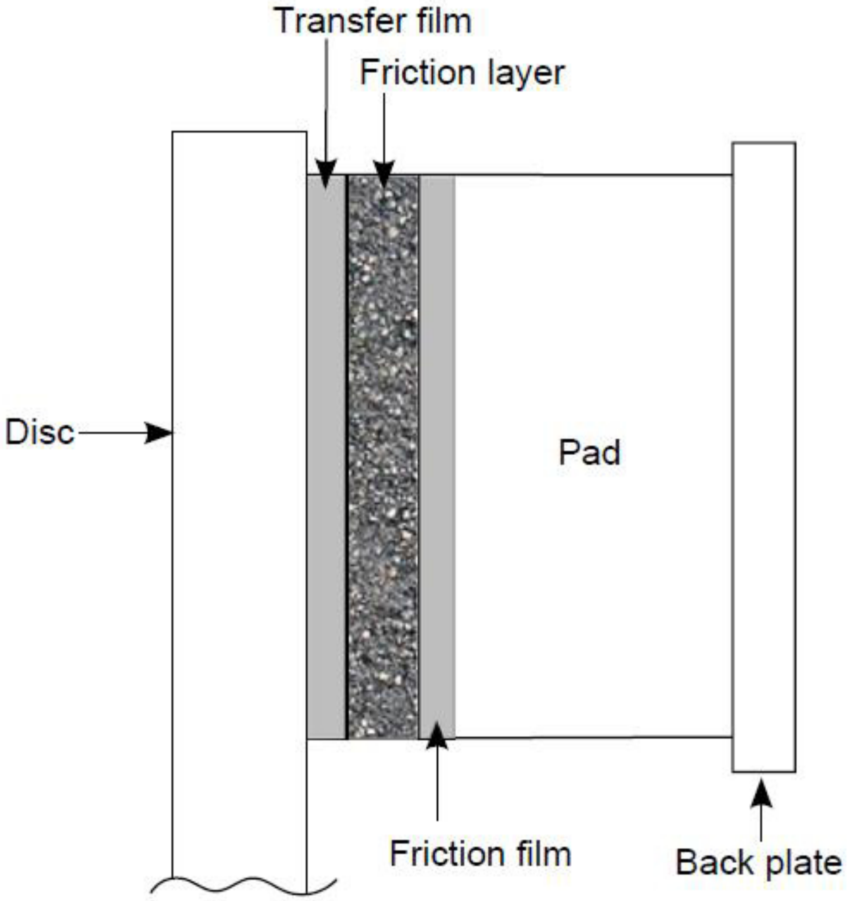


Figure I.IV: Mechanism of interface based on the layered structure of the third body [9]

Contact plateaus, **fig. I.III** consist of two parts, primary plateaus and secondary plateaus. The primary plateaus first form due to the lower removal rate of the mechanically stable and wear resistant ingredients of the pad. In a second stage, these protruding hard phases may form nucleation sites for the growth of secondary plateaus, piling up against the primary plateaus.

The secondary plateau is composed of the third body debris. The contact plateaus mechanism is observed in particular for low-met and semi-met brake pads, due to the high content of steel fibers, thanks to the good wear resistance of steel. [16, 17]

The second model is based on the idea that disc and pad are separated by a third body with a layered structure, **fig. I.IV**. The film that is deposited to the disc surface is called transfer film, the film on the pad surface is called friction film and the loose particles layer in the middle is called friction layer. Third body behaves as a "lubricant" so it permits to decrease the wear preventing the direct contact of pad with disc. A uniform transfer film on the disc permits to give a stable CoF at elevated temperature. The layered third body model is observed for the NAO based brake pads. [18, 19, 20]

The friction and wear behavior of a brake pad is primarily controlled by the formulation of the friction material. Ideally CoF should be independent on velocity and load. However temperature, velocity and force have an effect on CoF and wear. In general it's possible to observe how CoF and wear decrease with increasing temperature. Fade is the term used to describe the loss in braking behavior at elevated temperature (300-400°C) due to the reduction of friction coefficient μ. It is caused by the heat generated during braking phenomena and it is associate to the phenolic binder and organic compounds degradation. The return at the desired friction level at lower temperature is described as recovery.

Velocity has a similar effect on CoF and wear, due to the relation of speed with the energy converted into heat [5, 20, 21].

To conclude load has a different effect on CoF and wear. Increasing the load, the secondary plateaus area will increase, with a reduction in pressure so the wear rate will decrease. For friction coefficient, increasing force the elastic deformation of brake pad will increase. It causes an higher contact area with an increased CoF [17, 22, 23].

In any case it has not been found a relation between wear and friction coefficient. [24]

IV. Brake pads production process

Considering the modern system, on the base of the ITT Italia process, three different phases can be defined regarding the production of brake pads: dry mixing, hot molding and curing of friction materials. [10]

Dry Mixing: The mixing of the friction formulation is a process conducted in dry conditions. The mixing machines are usually equipped with blades and choppers, which permit with the good mixing of the friction formulation, an appropriate “opening” of chopped fibers, in particular kevlar fibers used to inhibits the segregation, due both to gravity and to electrostatics charge generated during the mixing.

Hot Molding: It is designed to achieve the resin-curing temperature. Usually working conditions are: temperature 120-180°C, molding times 3-7min, pressure 20-160MPa. The conditions depend on the pads size and resin reactivity. In **fig. I.V** it’s possible to observe the homogeneous heating system and the unidirectional pressing. The die presses the material on the back plate. The friction formulation is the first material inserted in the mold, followed by the underlayer formulation.

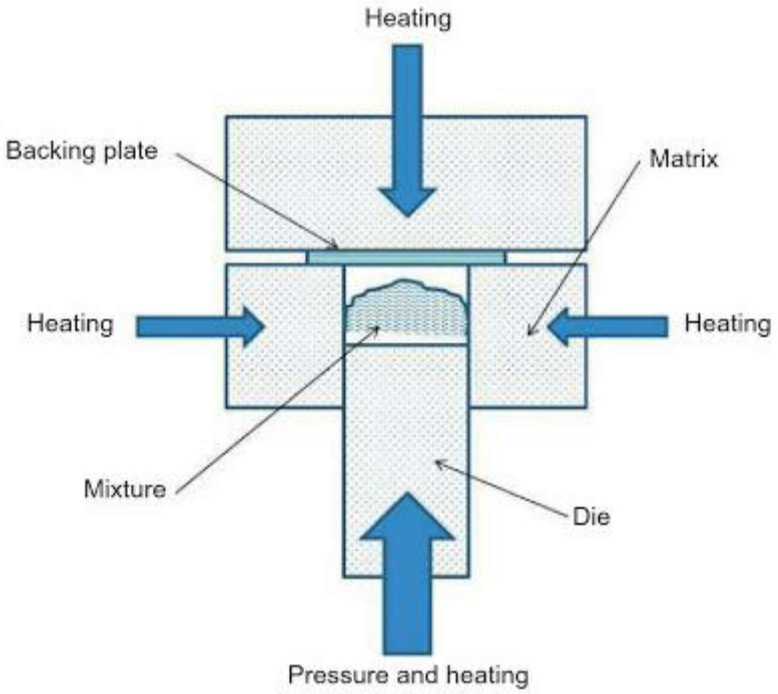


Figure I.V: *Molding region of a hot molding press [10]*

Curing of friction material: A thermal treatment in an inline IR oven is the most diffused system to have the complete curing of the phenolic resin in the friction materials. At the same time the cross-linking occurs for the underlayer resin. The IR curing permits also to have the stabilization of physical, mechanical and friction properties of the brake pads, because the pad's surface reach temperature in the order of 300°C like the medium working temperature of brake pads.

For brake pads based on geopolymer matrix, it will be shown how the curing step it's not required for the friction material, for the specific geopolymer composition investigated.

This is another strong aspect on the use of geopolymer, because it permits to decrease the environmental impact of geopolymer based brake pads.

V. Geopolymers

Geopolymers are inorganic materials, and the term was used for the first time by Davidovits in the late 1970's [25]. It's important to don't confuse the geopolymers with alkali-activated materials and cements which were originally developed by Glukhovsky in the Ukraine during the 1950s [26]. Davidovits worked predominantly with clays-based products and calcium-free system, in order to have a stable inorganic structure.

The chemical composition of geopolymer is quite similar to zeolite, with a microstructure variable from amorphous to crystalline, in function of the composition and the synthesis conditions. To have a stable structure, the negative charge of AlO_4^- tetrahedra has to be balanced from the positive ions present in the system. The complex geopolymer structure consists of chains, sheet-like and three-dimensional networks constituted of various Q unit types of connected SiO_4 and AlO_4 tetrahedra. Davidovits also classified the silicate and aluminosilicate materials in function of the Si:Al atomic ratio, see **table I.I** and **fig. I.VI.**

Si:Al ratio	Nomenclature
0	Siloxo
1	Sialate
2	Sialate-siloxo
3	Sialate-disiloxo
>3	Sialate link

Table I.I: Elementary units classified according to the Si:Al atomic ratio [27]

The atomic ratio Si:Al in the poly(sialate) structure controlled the network type of geopolymer, the properties and so the applications. A ratio lower than Si:Al < 3 gives a rigid 3D-network, and higher silicon content gives enhance the polymeric behavior.

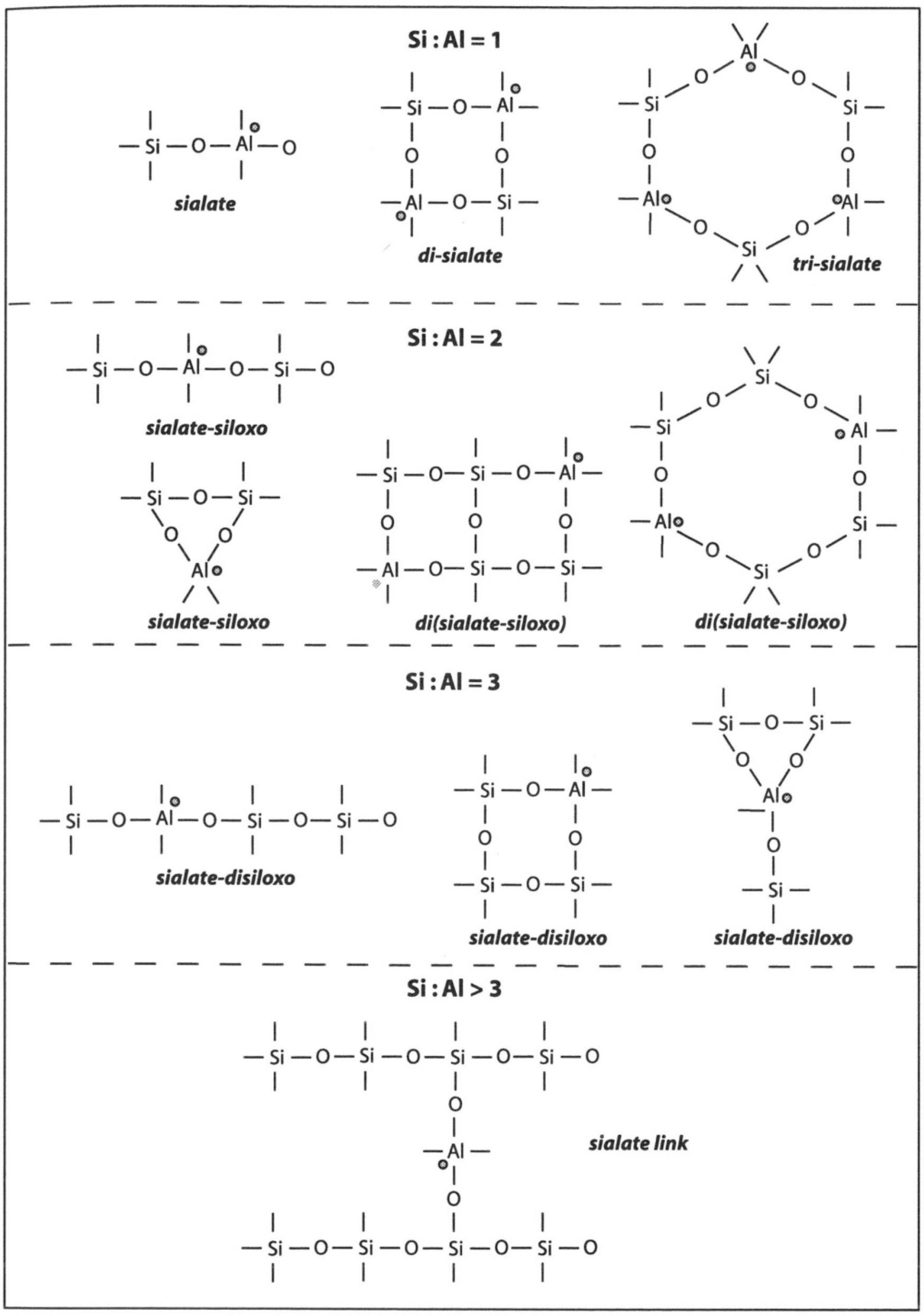


Figure I.VI: Terminology and structure of poly-sialate geopolymer, and applications [27]

For the geopolymerization it's possible to distinguish between two synthesis routes [27]:

- In alkaline medium (Na^+, K^+, Li^+, Ca^{++}, Cs^+ and the like);
- Mainly in acidic medium with phosphoric acid leading to poly(phosphor-siloxo) and poly(alumino-phosphor).

The synthesis happens between an aluminum-silicate source and an activating solution. The most diffused geopolymer are based on alkali system, in particular sodium and potassium based geopolymer. A typical example is the reaction between a dehydroxylated aluminum silicate (metakaolin) within an alkaline comprising hydroxides and alkali-silicates. The geopolymerization mechanism depends on the type of cations but can be generalized as in **fig. I.VII**

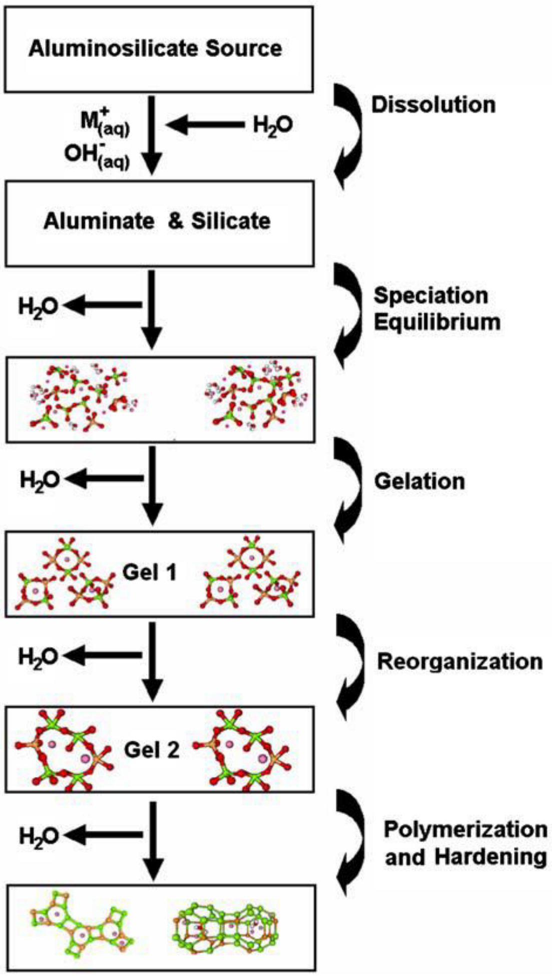


Figure I.VII: Phase of geopolymerization [28]

The reaction mechanism shows how the solid aluminosilicate source is converted into a synthetic alkali aluminosilicate.

Dissolution of the solid aluminosilicate by alkaline hydrolysis produces aluminate, silicate and aluminum-silicate species, in general ortho-sialate molecules. The dissolution consumed water (formation of -OH groups). Then the interaction between these molecules thanks to the alkaline solution leads to the polycondensation into oligomers (gelation) and polymer network (solidification and hardening). This process releases the water that was nominally consumed during dissolution. Water plays the role of a reaction medium but resides within pores in the gel. The reactivity of aluminum in the system can be tuned by fine grinding of raw materials or heat treatment. [28]

Materials generated by the alkaline activation of metakaolin and/or fly ashes constitute a unique family of materials of a mixed nature, with properties varying from those characteristics of cements, ceramics and zeolites (depending on formulation).

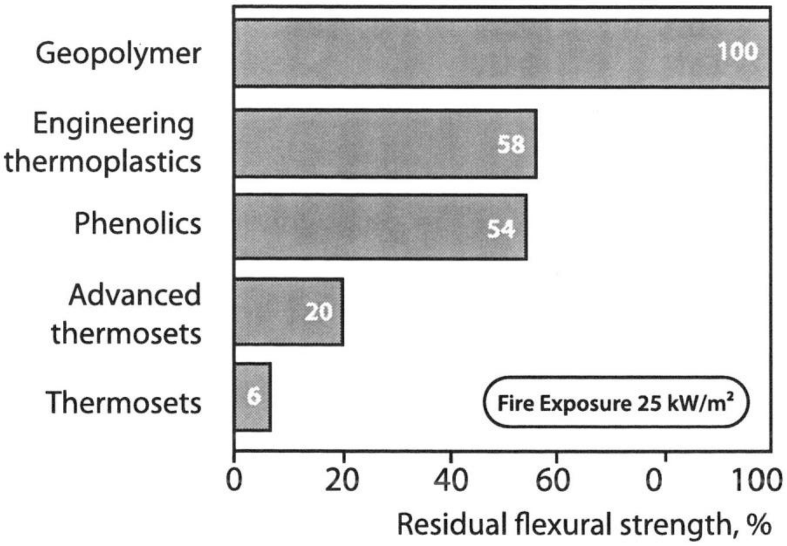


Figure I.VIII: Residual flexural strength of cross-ply laminates after fire exposure thermal [27]

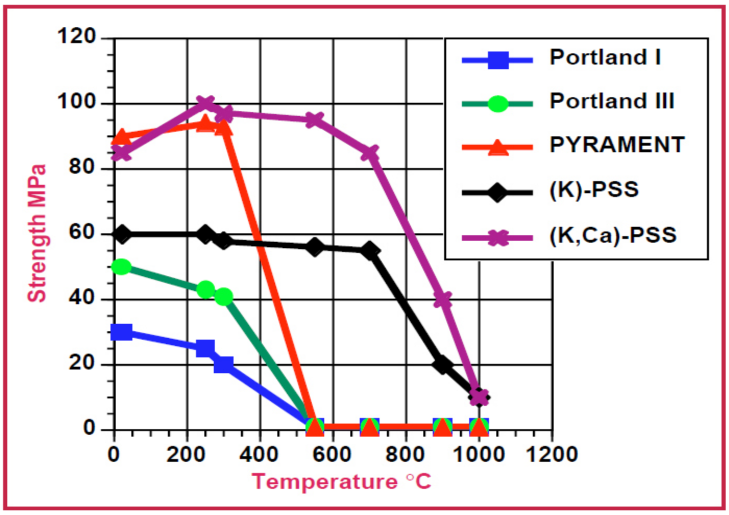


Figure I.IX: Strenght retentions at elevated temperatures of ordinary Portland cement compared with geopolymer cement (K-PSS and (K,Ca)-PSS) [25]

The primary area of application of geopolymers is currently in the development of low-CO_2 construction materials as a greener alternative to Portland-based cements; they can provide other

technological advantages over traditional construction materials. Also, for the case of geopolymer concrete derived from fly ash, the cost of the material is generally lower than OPC by a factor of about 10–30%. Other applications include host matrix in waste encapsulation, as a low-cost ceramic (either used directly or as a precursor for calcination), fire protection of structure, bricks, tooling for Al SPF, and heat resistant composites to 1000°C. [27]
The geopolymers have similar mechanical properties to cements and organic resins, but a better thermal resistance than organic resins (in particular phenolic resins) and cements as shown in **fig. I.VIII** and fig. **I.IX**. In fact:

- As discussed for fade, organic resins decompose by oxidation starting from 300-400°C.
- For Portland cements, starting from ~300°C water is released from CSH causing the loss in mechanical properties.

We do the comparison with Portland cement and not only with phenolic resin, because hydraulic binders have been considered as a potentially substitution of phenolic resin. In fact, an European project "Cobra Project" has been financed to investigate this possibility. [29] So we decided to investigate geopolymers as matrix for brake pads because they have not yet been considered as a potential matrix and thanks to their good thermal resistance should possess a fade behavior better than organic resins and Portland cement. Moreover geopolymer possess better carbon footprint and lower water consumption compared to phenolic resins and ordinary cements.

1-EXPERIMENTAL PROCEDURES AND CHARACTERIZATION TOOLS

1.1 Raw materials

It was possible to produce the geopolymer components and geopolymer based brake pads, because we had the consolidation of the geopolymer system. The details of the geopolymer compositions and synthesis will be described on the next chapters, but in general to produce the brake pads we worked in dry conditions starting from geopolymer-precursor raw materials, or geopolymer powder.

The raw materials used to produce the geopolymer matrix was: deionized water, sodium hydroxide and sodium silicate to prepare the activating solution or as alkali sources, like the NaOH. Kaolin and metakaolin were used as alumino-silicate sources. For the raw materials used to produce the geopolymer matrix of the brake pads, the commercial name and the composition are reported in **tab. 1.1.**

	Sodium hydroxide Chimica Strola	Sodium silicate PQ Corporation	Metakaolin Imerys Argical 1200s	Kaolin Aprochimide
Na_2O (%wt)	22-23	19-26.5	/	/
SiO_2 (%wt)	/	53-61	55	48-50
Al_2O_3 (%wt)	/	/	39	36-37
H_2O (%wt)	76-77	20	/	12.5-13
Other (%(wt)	<1	<1	6	1.2-1.4

Table 1.1: Composition of raw materials used to produce geopolymers

We did not consider other cheap alumino-silicate source as fly ash (a waste material typically used for geopolymer), because kaolin and metakaolin are natural derived materials so they permit to have a composition constant with time, in order to have an appropriate control on the quality of the geopolymer system. To grind and to mix the raw materials the ball milling technology was used.

1.2 Production of geopolymer components and brake pads

On the base of the industrial process production of brake pads based on phenolic resin described on background chapter, to produce geopolymer components a lab-scale hot molding dry process technology was used.

Figure 1.1: Short time reaction machine, Struers Prontopress-2, with details of pressing region

For short reaction/pressing time we used a warm press machine, Struers Prontopress-2, **fig. 1.1**. On the machine it was possible to control the temperature, pressure, heating and cooling time.

The molding region is in stainless steel and samples with a diameter of 40mm and variable thickness were obtained. In general, with this system we will change the heating time. The cooling time will be fixed at 4 min for all the test described in the thesis work.
For long reaction/pressing time a warm pressing frame was used, **fig. 1.2**. Using spring it was possible to maintain a stainless-steel mold on pressure. The hot molding step was done putting the frame in an oven. Samples with a diameter of 50mm were obtained.

Figure 1.2: Warm pressing frame for long pressing time

With the frame system, it was not possible to evaluate the real value of pressing time for the components. The limit was related to the fact that the heating speed of the mold was lower than the heating ramp of the oven. Fixing an oven treatment at 10°C/min to 150°C with a dwelling of 90min, for the geopolymer components we considered a pressing time of 60min at 150°C. The two systems permitted to work in the pressure range of 15 – 40 MPa, so the typical pressure range used for the production of brake pads. For the project, a pressure value of 20MPa was selected for the geopolymer reaction or consolidation.

To produce the geopolymer-based brake pads we used the pressing machines of the R&D department of ITT Italia, **fig. 1.3**. These machines were used to produce brake pads batches of a reduced amount, when the low production volume does not require to use the automatic industrial system. Compared with the laboratory pressing system, the R&D machines permitted to work with a degassing step during the molding, if required.

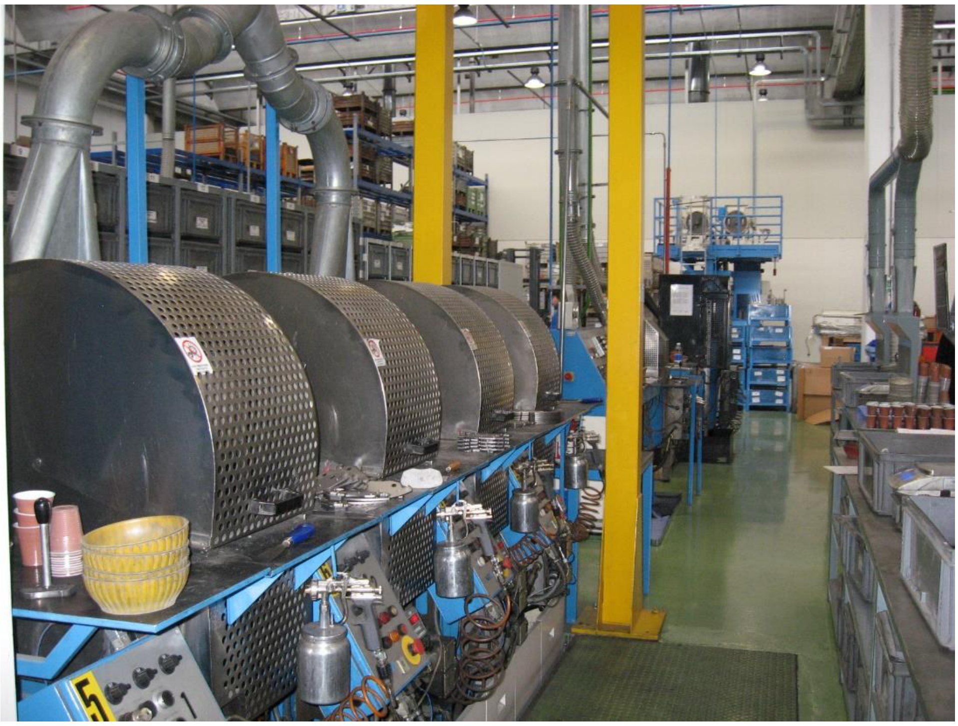


Figure 1.3: Pressing machines of ITT Italia R&D department

To mix the geopolymer matrix with the other materials of the friction formulations, semi-industrial machines have been used as Eirich and Loedige systems of the R&D department. This type of mixer machines is studied to work in dry conditions and to permit a homogeneous distribution of the ingredients used for the friction formulation.

Regarding the underlayer used for the geopolymer based brake pads, with ITT different tests have been done, to evaluate the commercial ITT underlayer composition, which possessed the best compatibility with the geopolymer based friction material. The composition of the underlayer cannot be reported due to intellectual property of ITT Italia. We used the same underlayer composition for all the geopolymer system developed during the project. The underlayer is also prepared by dry mixing of the phenolic resin with rubber, steel fibers and other components to ensure damping properties of the pads.

1.3 Characterization of the geopolymer components

For the studies of the geopolymer synthesis and to follow the geopolymer reaction XRD, ATR-FTIR and NMR analysis have been carried out as main methods.

- The X-ray diffraction analysis permits to evaluate the crystalline structure of geopolymer system. This technique is important in particular when we have the formation of a crystalline geopolymer, called zeolite. XRD analysis in fact permits a fast and nondestructive analysis on the surface of the brake pads. X-Ray diffraction analysis (D8 Advance, Bruker Italia Srl, Milano, IT) was performed on powdered geopolymer samples and on brake pads with Cu Kα radiation (10–70° 2θ, 3 s/step).
- For amorphous geopolymer ATR-FTIR and NMR permit to evaluate the chemical structure of the geopolymer matrix, in particular if the aluminum is in coordination 4 as $AlO4^-$ tetrahedra, in order to certify the stability of the geopolymer matrix. [27] The FTIR spectra are collected with the instruments Spectrum One, Perkin Elmer. MAS-NMR analysis were obtain using a Varion 400 Spectrometer, 4mm rotor, 2s delay time. ^{27}Al: 104.32MHz, 400 scans and 10kHz of MAS-rate, $Al(NO)_3$ as reference ^{29}Si: 79,53MHz, 1800scans, 12kHz MAS-rate, Q8M8 as reference

To evaluate the properties of the pure geopolymer components morphology, microstructure, porosity, compressive strength and the Brazilian test resistance have been evaluated. In particular:

- The morphology and microstructure of the samples were investigated using an optical stereoscope (STEMI 2000-C, Carl Zeiss AG, Oberkochen, DE) and a scanning electron microscope (ESEM, Quanta 200, FEI, Hillsboro, OR).
- The true density of the ground geopolymer was measured with a helium pycnometer on finely crushed powders (Accupyc 1330, Micromeritics, Norcross, GA). As it will be described for each geopolymer compositions we worked in dry condition using powder able to consolidate. So, on the base of preliminary results, we did the hypothesis of total open porosity for geopolymer matrices. By the measure of the geometrical density we estimated the total porosity.
- The compressive strength has been done to evaluate the differences between various geopolymer composition. The sample have a dimension of 10x10x10mm^3. The

compressive strength was measured at room temperature using an Instron 1121 UTM (Instron Danvers, MA) at cross-head speed of 1 mm/min.

- The Brazilian test has been used to evaluate the effect of a parameter on a defined geopolymer composition. The Brazilian test is the diametral compressive test and it is conducted on a disc, **fig. 1.4**. It is and indirect way to estimate the tensile strength of an isotropic brittle material, but without the problem of a direct tensile strength test that for ceramic is not commonly used. Moreover, we selected this test because the pressing machines permitted to obtain disc suitable for the test and without any shaping process. The test was done at room temperature using an Instron 1121 UTM (Instron Danvers, MA). The standard [30] required a load speed system, but the machines permits to control the cross-head speed. From preliminary test we found that with a cross-head speed of 20 mm/min the load speed was comparable to normative requirements.

  The test has been introduced by Carneiro [31,32] and Akazawa [33] and could be applied for isotropic materials. The equation to determine the Brazilian resistance is:

$$\sigma_t = \frac{2P}{\pi D t} \tag{1}$$

  Where P is the load, D the disc diameter and t the thickness. The formula gives the tensile stress perpendicular to the loaded diameter at the center of the disc at the time of failure when the applied force is P. Failure initiates at the center of the core (where the ratio of compressive to tensile stress is least and equals three) and propagates outward along the loading direction, **fig. 1.4**.

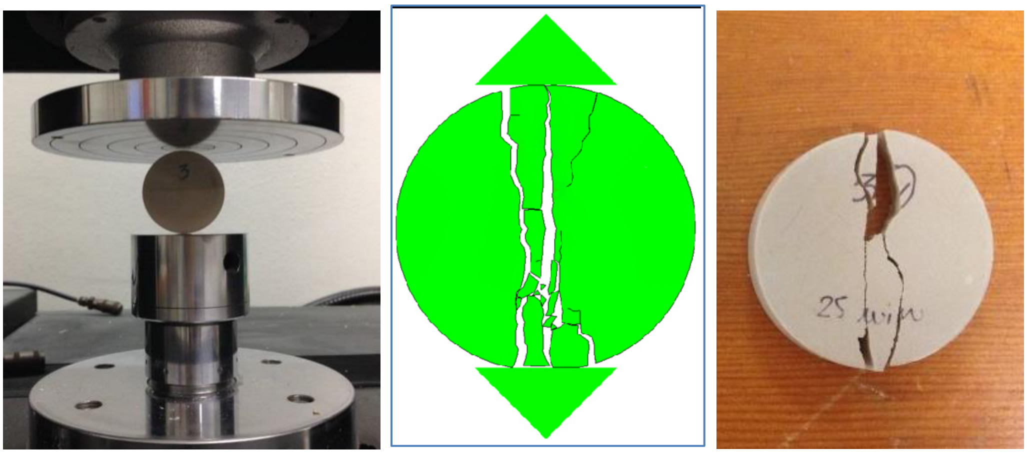


Figure 1.4: Brazilian test setup (left), isotropic material ideal fracture pattern [34](center), geopolymer components failure pattern (right)

For anisotropic and in particular for layered materials [35], the Brazilian test can be used to evaluate the main principal symmetry direction of the material, looking to the failure mechanism in function of the foliation-loading angle, **fig 1.5**.

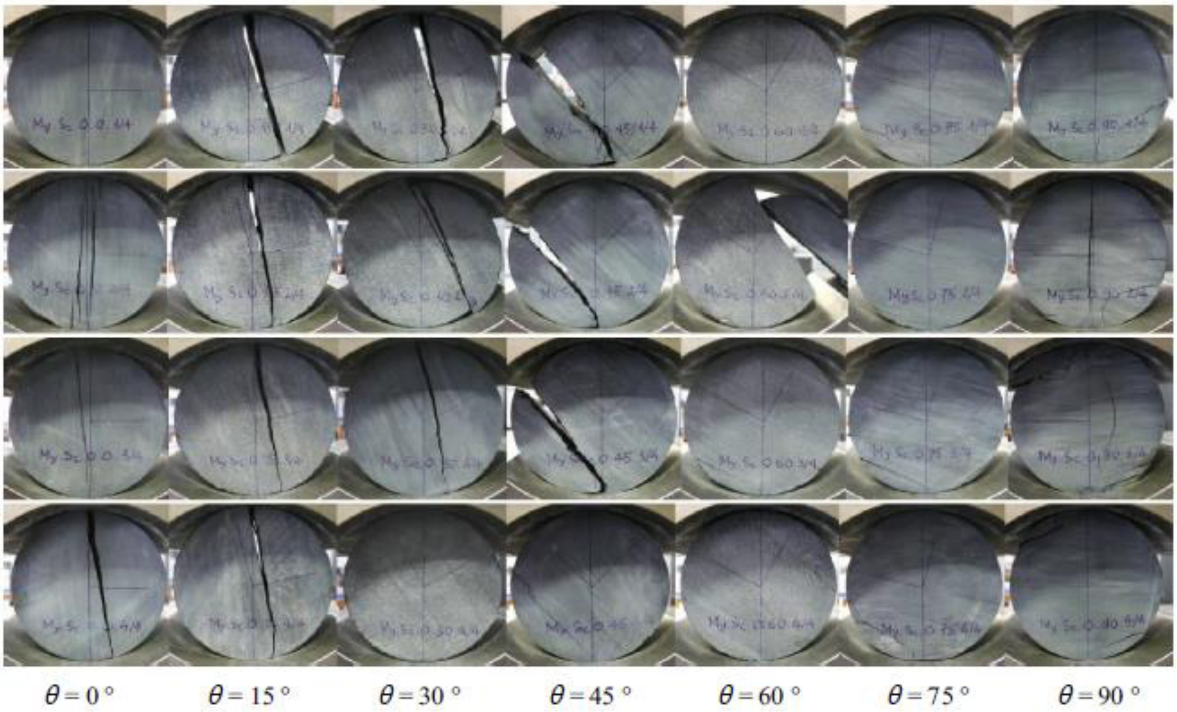


Figure 1.5: Fracture patterns of Mosel slate disc under different foliation-loading angles [35]

1.4 Characterization of geopolymer-based brake pads

For the project, brake pads of a "Segment B (European classification)"[36] vehicle have been used as format for the study. The choice has been taken in collaboration with ITT Italia to investigate the use of geopolymer in one of the most important vehicle market.

To characterize the brake pads and in particular the friction material, three friction/wear test have been considered: AK-master, AKM-TL110, Krauss-Wolverine test. The conditions for the test depend on the geometry of the pad and the inertia of vehicle. In particular the resistance of the brake pads to different energy test, and the friction coefficient in various conditions were evaluated. We did not consider general wear and friction evaluations in terms of laboratory measure like ball-on-disc because in laboratory we developed the geopolymer matrix, but no composites material.

AK-Master test: It’s a test used to evaluate the behavior of brake in normal braking event. The dynamometer permits lab testing of the brake of a vehicle in real size. Control may be of the following type: pressure, torque, force, position and mixed. Braking is recorded and analysed in terms of braking moment, pressure, pump stroke and temperature (of the disk, friction material and brake fluid).

Step n°	***Step name***	**description**
1	*Green μ Characteristic*	30 snubs 80 to 30 km/h at 3 000 kPa
2	*Burnish*	64 snubs 80 to 30 km/h at varying pressures
3	*Characteristic Value 1*	6 snubs 80 to 30 km/h at 3 000 kPa
4.1	*Speed/pressure sensitivity 40 km/h*	8 stops 40 to 5 km/h at increasing pressures
4.2	*Speed/pressure sensitivity 80 km/h*	8 snubs 80 to 40 km/h at increasing pressures
4.3	*Speed/pressure sensitivity 120 km/h*	8 snubs 120 to 80 km/h at increasing pressures.
4.4	*Speed/pressure sensitivity 160 km/h*	8 snubs 160 to 130 km/h at increasing pressures.
4.5	*speed/pressure sensitivity 200 km/h*	8 snubs 200 to 170 km/h at increasing pressures
5	*Characteristic Value 2*	6 snubs 80 to 30 km/h at 3 000 kPa
6	*Cold Application*	1 stop 40 to 5 km/h at 3 000 kPa
7	*Motorway Applications*	1 stop and 1 snub at 0.6 g
8	*Characteristic Value 3*	6 snubs 80 to 30 km/h at 3 000 kPa
9	*Fade 1*	15 stops 100 to 5 km/h at 0.4 g and increasing initial temperatures 100 to 550°C log scale
10	*Recovery 1 (Characteristics values)*	18 snubs 80 to 30 km/h at 3000 kPa
11	*Temperature/Pressure Sensitivity 100 °C*	8 snubs 80 to 30 km/h at increasing pressure, initial braking temperature < = 100 °C
12.1	*Increasing temperature 500 °C*	9 snubs 80 to 30 km/h at increasing temperature
12.2	*Pressure line 500 °C*	8 snubs 80 to 30 km/h at increasing pressure, initial brake temperature < = 500°C
13	*Recovery 2 (Characteristics values)*	18 snubs 80 to 30 km/h at 3000 kPa
14	*Fade 2*	15 stops 100 to 5 km/h at 0.4 g and increasing initial temperatures 100 to 550°C log scale
15	*Recovery 3 (Characteristics values)*	18 snubs 80 to 30 km/h at 3000 kPa

Table 1.2: SAE J2522 (AK-Master) testing procedure

A typical example for AKM procedure is the SAE J2522, which is described in **tab. 1.2.** Different regions in the graphic report can be defined to evaluate a specific behavior of the brake pad. However, for the project we compared the main results of the AK-master test to compare the geopolymer based brake pads with the commercial products, and in particular it has been focused the attention on the fade region of the test. In **fig. 1.6** are shown the case and the AK Master dynamometer system. The temperature was measured with thermocouples at the friction path centre radius 0.5 mm ± 0.1 mm deep in the disc outer face.

Figure 1.6: Case and dynamometer used for AK Master test

AKM – TL110 test: The TL-110 test was conducted on the same pads which was subjected to the AK-Master test. The TL-110 test is a wear test on the pads and disc. It consists of 500 brake cycle with fixed temperature at a constant torque/deceleration and for the test is used the same dynamometer used for the AK master characterization.

Krauss-Wolverine test: It's a safety test which is required to ensure the resistance of the brake pads to high energy braking event. During the test, after a heating step, a series of braking was performed to maintain the pads temperature at a desired value for a defined time. The most energetic conditions required to brake to reach a disc temperature of 600°C and to maintain it for 15min by braking. For the test it's considered the friction behavior during the test. It is also important for the success of the test, to have the integrity of the pad at the end of the test. The system of Krauss-Wolverine test is reported in **fig. 1.7**. It is a simple system because it has not to work with different torque value.

Figure 1.7: Krauss-Wolverine dynamometer machine

2-SODALITE BASED BRAKE PADS

Partially published in:

Sin A, Angeleri A, Lupone F, Caldarola D, Conte A, Colombo P.: Friction material, in particular for the manufacturing of a brake pad, and associated preparation methods. Eur. Patent Application 3128201, filed 2015/07/14

To develop a geopolymer based friction formulation, a first geopolymer composition based on a hydrothermal synthesis has been studied, called Siliface process. On the base of this system a geopolymer composition able to react in absence of water has been developed and used as matrix to produce brake pads.

2.1 SILIFACE PROCESS

The Siliface process [27] [37] is one of the first milestone in geopolymer technology. It is also called solid state synthesis of Na-PS blockpolymers, related to the ultra rapid in situ transformation of kaolinite in hydrosodalite, **fig. 2.1**.

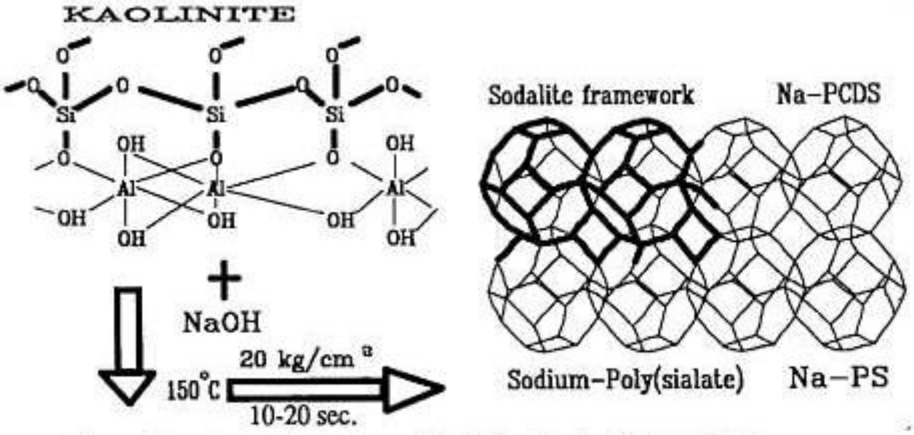


Figure 2.1: Ultra rapid (10-20sec.) in situ transformation of kaolinite in Na-PS Hydrosodalite, under pressure at 150°C [27]

Different patents and publications described the process and the conditions required to have the reaction. To understand the system, and to evaluate the feasibility of the application of Siliface process to the production of brake pads, we looked the process details: [38][27]

- Natural aluminosilicates in power form are mixed with powdered **NaOH** in the proportion of 1 mol or less of **NaOH** for 0,5 mol **Al_2O_3**.

- This mixture is moistened to a water content of 6-15% of the initial powdered mixture or 1 g **water** for 1-1.5 g NaOH.

- The resulting granules are ground up and the semi-dry powder is placed in a cold mould and **pressed under 150 kg/cm^2.**

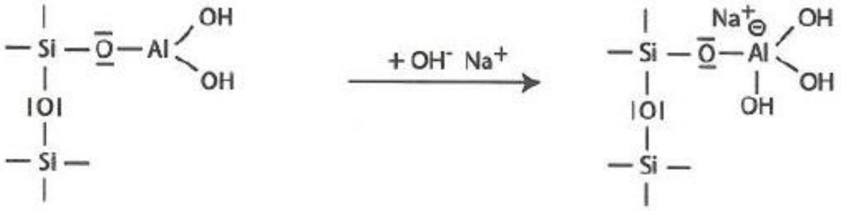
- The resulting crude plates are placed under a heated press equipped with pervious systems enabling water evaporation during the thermosetting phase. **Thermosetting parameters** are:
- **temperature:** 130°C to 200°C
- **pressure:** higher than the saturated vapour pressure (svp) of water, i.e. 10 to 30 kg/cm^2
- **time:** one minute per millimetre thickness.

The followed sodalite reaction mechanism comes from : "J. Davidovits, Geopolymer - Chemistry and applications 2011" [27]

"For the hydrosodalite synthesis a covalent bond mechanism has been proposed under the hydrothermal conditions:

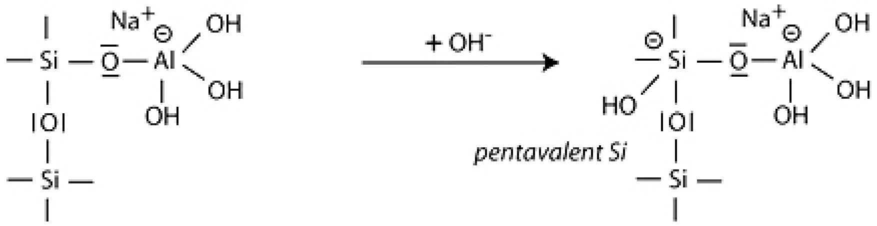
1) *Alkaline depolymerization of the poly(siloxo) layer of kaolinite*
2) *Formation of the ortho-sialate $(OH)_3$-Si-O-Al-$(OH)_3$ molecule*
3) *Polymerization (polycondensation) into higher oligomers and polymers*

***Step 1**: alkalination and formation of tetravalent Al in the side group sialate -Si-O-Al-$(OH)_3Na^+$,*



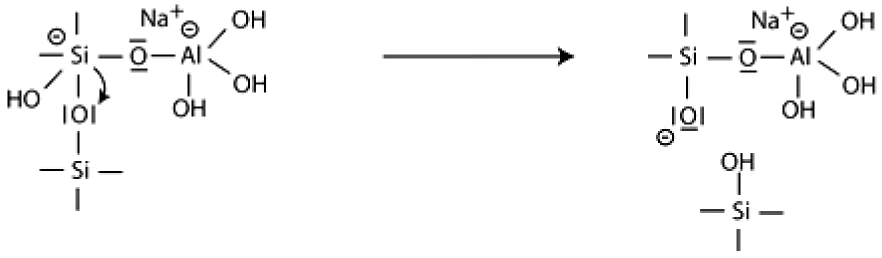
(1)

***Step 2**: alkaline dissolution starts with the attachment of the base OH- to the silicon atom, which is thus able to extend its valence sphere to the penta-covalent state,*



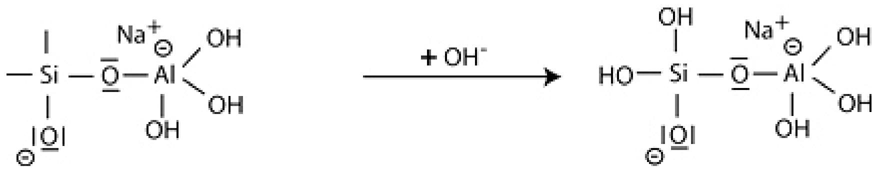
(2)

***Step 3**: the subsequent course of the reaction can be explained by the cleavage of the siloxane oxygen in Si-O-Si through transfer of the electron from Si to O, formation of intermediate silanol Si-OH on the one hand, and basic siloxo Si-O- on the other hand.*



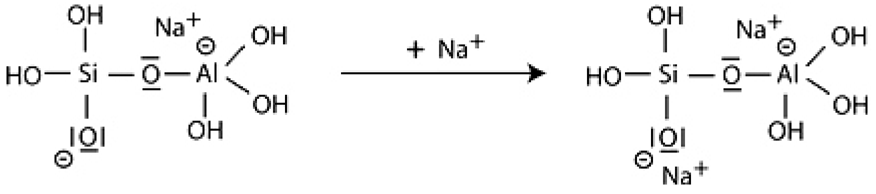
(3)

***Step 4**: further formation of silanol Si-OH groups and isolation of the ortho-sialate molecule, the primary unit in geopolymerization.*



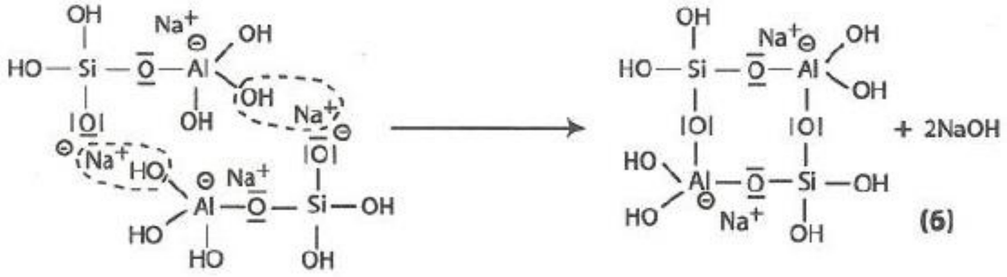
(4)

***Step 5**: reaction of the basic siloxo Si-O- with the sodium cation Na^+ and formation of Si-O-Na terminal bond.*

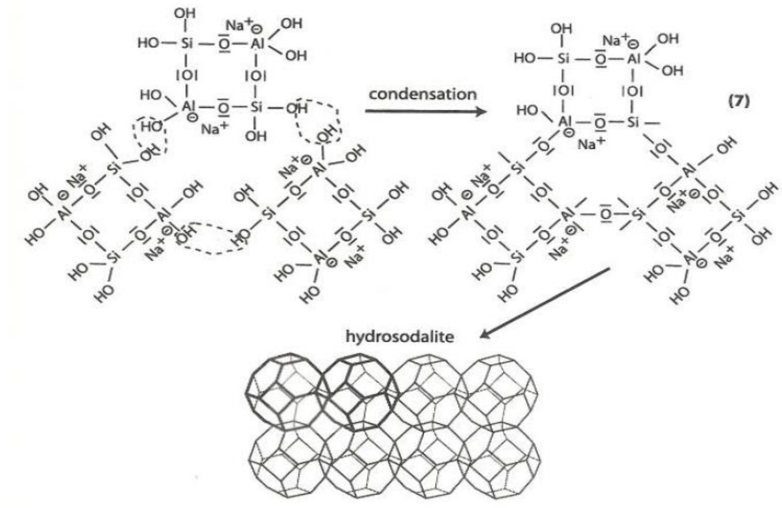


(5)

***Step 6**: condensation between ortho-sialate molecules, reactive groups Si-ONa and aluminum hydroxyl OH-Al, with production of NaOH, creation of cyclo-di-sialate structure, whereby the alkali NaOH is liberated and reacts again.*



Step 7*: polycondensation of 3 cyclo-disialate into hydrosodalite network, Na-poly(sialate), Na-PS with quadratic and hexagonal sub-units.* ***Si:Al=1:1”***



The Siliface process was considered interesting for the production of a geopolymer matrix for brake pad, because looking to the condition required for the crosslinking of phenolic resin and so for the production of brake pads, the Siliface process had comparable conditions. Also, the Mohs hardness of hydrosodalite is 5.5-6 so comparable with the medium abrasive used in brake pads. But considering the brake pads production technology described in background, two main differences can be found:

1. The use of water required to modify the mold structure, because the steam generated during the pressure had to be eliminated to have a good densification of brake pads
2. The mixing process of friction formulation occurs in dry condition. For the Siliface process a paste with a variable water content (6-15%wt) has to be formed before the molding step and mixed with the raw materials of friction formulation.

But as described in the introduction, the guidelines from ITT Italia were to develop a geopolymer system that didn't require any modification on the process technology. For this reason, a dry Siliface process has been developed.

It's important to observe how the Siliface process gives the formation of a crystalline material, but normal geopolymer are amorphous materials. Geopolymer can be considered as "proto-zeolites", so materials able to develop zeolite structure thanks to pressure and temperature. Moreover, hydrosodalite possess the "ideal" composition to have a stable geopolymer structure, because the Na/Al ratio is equal to 1.

Temperature and water content are generally higher in zeolite synthesis systems than in geopolymerization, but there is no clear distinction between the conditions under which, each product is obtained. [39]

2.2 DRY SILIFACE PROCESS

2.2.1 Preliminary test

With the limitation to cannot use water to mix kaolin and sodium hydroxide with the raw materials of the friction formulation, we did some tests working with the pure geopolymer system, to evaluate if it was possible to have a hydrothermal reaction in absence of water. For the test we considered the kaolin-sodium hydroxide ratio reported for the Siliface process: "Natural aluminosilicates in powder form are mixed with powdered NaOH in the proportion of 1 mole or less of NaOH for 0,5 mole Al_2O_3". [37]

The ratio described was stoichiometric to the Sodalite $Na_6Al_6Si_6O_{24}\cdot xH_2O$. In fact, many type of sodalite species can be defined in function of the chemical bonded water. [39]

For the test commercial kaolin (Aprochimide) and sodium hydroxide (Chimica Strola) were used. The stoichiometric NaOH/kaolin ratio was 2:1.

The mixture kaolin-NaOH was prepared in two different steps: first the NaOH powder was produced by ball milling at 450 rpm for 30min. The mixing of NaOH powder and kaolin was conducted by ball milling at 300 rpm for 30min. The kaolin was introduced on the jar with ground sodium hydroxide and respecting the ratio Na/Al =1.

In order to simulate a pressing system similar to the Siliface process, and in order to enhance the reaction due to the absence of water, we used the warm pressing frame described for long pressing time reaction §1.2. So, a hot molding at 150°C for 1h and 20MPa was performed. The XRD analysis on powder of the ground components is shown in **fig. 2.2.**

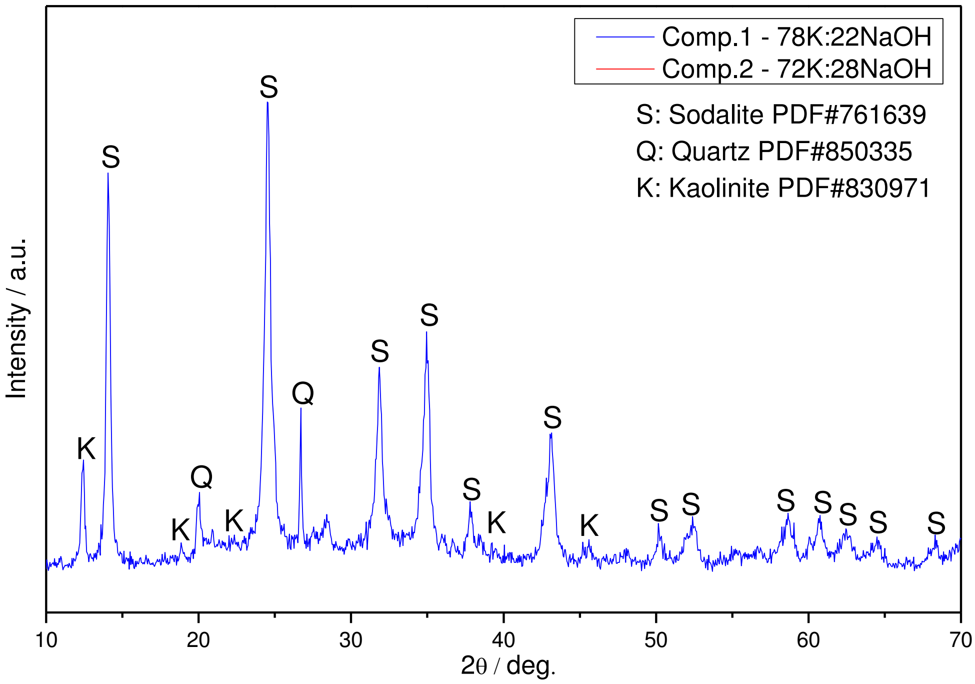


Figure 2.2: XRD analysis of a sample pressed at 20MPa 150°C for 60min with Na/Al =1

It was possible to observe the formation of a basic sodalite $Na_8Al_6Si_6O_{24}\cdot(OH)_2\cdot(H_2O)_2$ PDF#761639, richer in Na than expected and with a Na/Al ratio of 1.33. For the ratio Na/Si the value was 1.33 because the ratio Si/Al=1, due to the kaolin composition. A small signal of quartz PDF#850335 was found, related to a kaolin impurity. No residual sodium hydroxide was detected. So we can say which it was possible to have an hydrothermal synthesis in dry condition, because water was not present at the beginning of the pressing process. This was the key point of our research, because we found a dry system which permits to have the formation of an inorganic matrix, working in condition similar to the brake pads production technology. Comparing the reaction of Siliface and "dry" Siliface process, for the dry process a NaOH/kaolin=2 did not permit to convert completely the kaolin/NaOH system into basic sodalite. (kaolin = $Si_2O_5Al_2(OH)_4$)

Siliface process reaction

$$6NaOH + 3Si_2O_5Al_2(OH)_4 \rightarrow Na_6Al_6Si_6O_{24}\cdot 6H_2O + 3H_2O$$

"Dry" Siliface process reaction

$$6NaOH + 3Si_2O_5Al_2(OH)_4$$
$$\rightarrow \frac{6}{8}Na_8Al_6Si_6O_{24}\cdot(OH)_2\cdot(H_2O)_2 + \frac{21}{4}\,H_2O + \frac{3}{4}\,3Si_2O_5Al_2(OH)_4$$

It meant that for the dry system, a residual kaolin remained at the end of the process.
In order to have the complete conversion of kaolin into basic sodalite the stoichiometric of the reaction has to be:

$$8NaOH + 3Si_2O_5Al_2(OH)_4 \rightarrow Na_8Al_6Si_6O_{24} \cdot (OH)_2 \cdot (H_2O)_2 + 8\, H_2O$$

2.2.2 Dry process kinetics study

To evaluate the effect of the composition on the kinetics of the reaction we considered different conditions. However to simplify the study, we decided to fix the pressure and temperature and to work only on time and composition, because we would to work with the lowest possible amount of sodium hydroxide, due to the alkalinity and hygroscopicity of sodium hydroxide, so to minimize the water absorption in order to work in dry condition.

1. For pressure and temperature typical values for brake pads production have been considered: T = 150°C and P = 20MPa
2. For time we studied the reaction at: 4,7,10,20,60min
3. For Composition we selected two ratio:
    1. Composition n° 1: (Reference hydrosodalite) 2 mol NaOH : 1 mol Kaolin
    2. Composition n° 2: (Reference basic sodalite) 8 mol NaOH : 3 mol Kaolin

So during the hot molding for the dry process, the reaction is:

$$a\, NaOH + b\, Si_2O_5Al_2(OH)_4 \rightarrow Na_8Al_6Si_6O_{24} \cdot (OH)_2 \cdot (H_2O)_2 + x\, NaOH + y\, Kaolin + z\, H_2O$$

Where: for composition n°1: a = 2 and = 1 and for composition n°2: a = 8 b = 3
and x,y,z depends on the pressing time

To fabricate the geopolymer components, for time of 4,7,10,20 min we used the short time pressing machine §1.2, for 60min reaction we used the long time pressing frame §1.2 used for the preliminary investigations.
To have samples with the same thickness independently on the diameter, 15g of powder were pressed for warm pressing machine (40mm) and 24g of powder for the warm pressing frame. The samples produced with the warm pressing machines are reported in **fig. 2.3 and 2.4.**

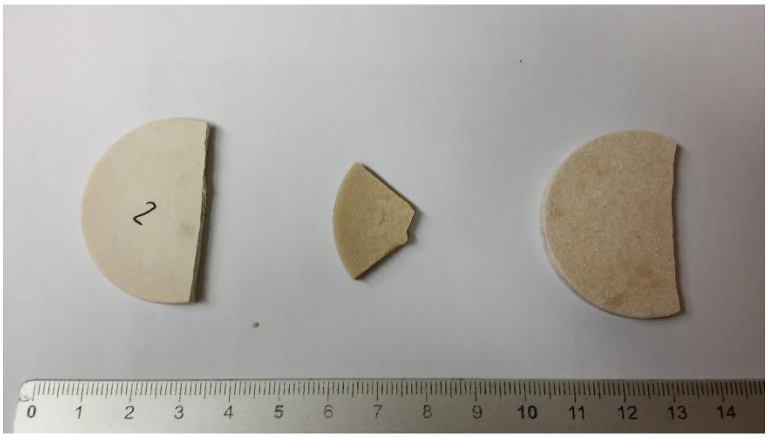


Figure 2.3: Hot pressed samples for Composition N°1: 4min (left), 7min (center), 10min (right)

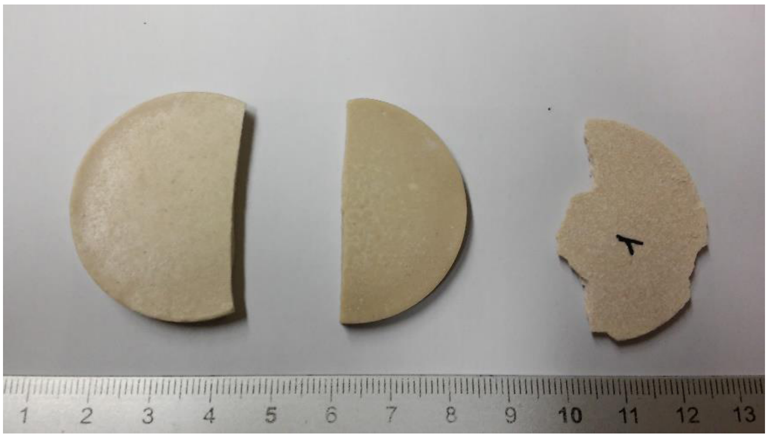


Figure 2.4: Hot pressed samples for Composition N°2: 4min (left), 7min (center), 10min (right)

A sample produced with the warm pressing frame is shown in **fig. 2.5.**

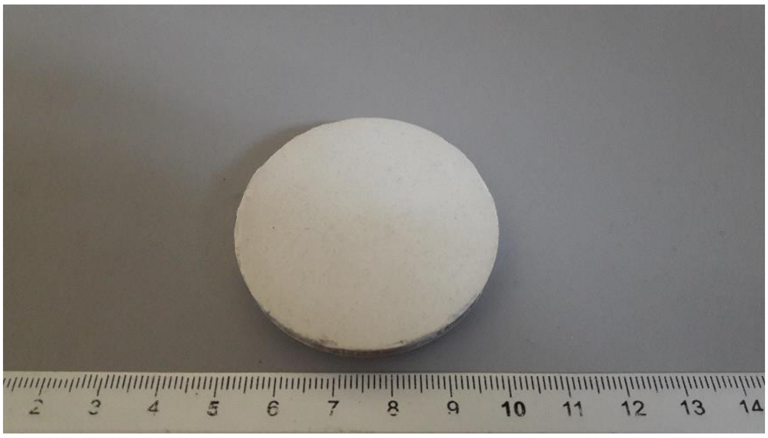


Figure 2.5: Hot pressed sample for Composition N°2: 60min

With the pressing frame it was possible to produce free cracks sample, independently on the composition. The samples obtained with the pressing machines were not free cracks. The reason was associate to the reaction. During the reaction water was produced as by-product.

The machine did not permit to eliminate the water as requested from the Siliface process, so the pressure associated to water steam caused the formation of cracks.

For the pressing frame the situation was different, because the mold possesses an integrated degassing system. In fact the geopolymer component were cracks free.

So it has been possible to measure the geometrical density and flexural strength only for the long time pressed samples, the less important in terms of production interest. No differences were observed for the two compositions considering a pressing time of 60min. A medium true density value of 2.2g/cm^3, a total porosity of 10%vol/vol and 4point bending test of 30-40 MPa were evaluated.

Despite of the limit of the warm pressing machine on the determination of the physics and mechanical properties of geopolymer components, we carried out the XRD analysis to evaluate the conversion of the reaction. The main results are reported in **fig. 2.6, fig. 2.7** and **fig. 2.8**.

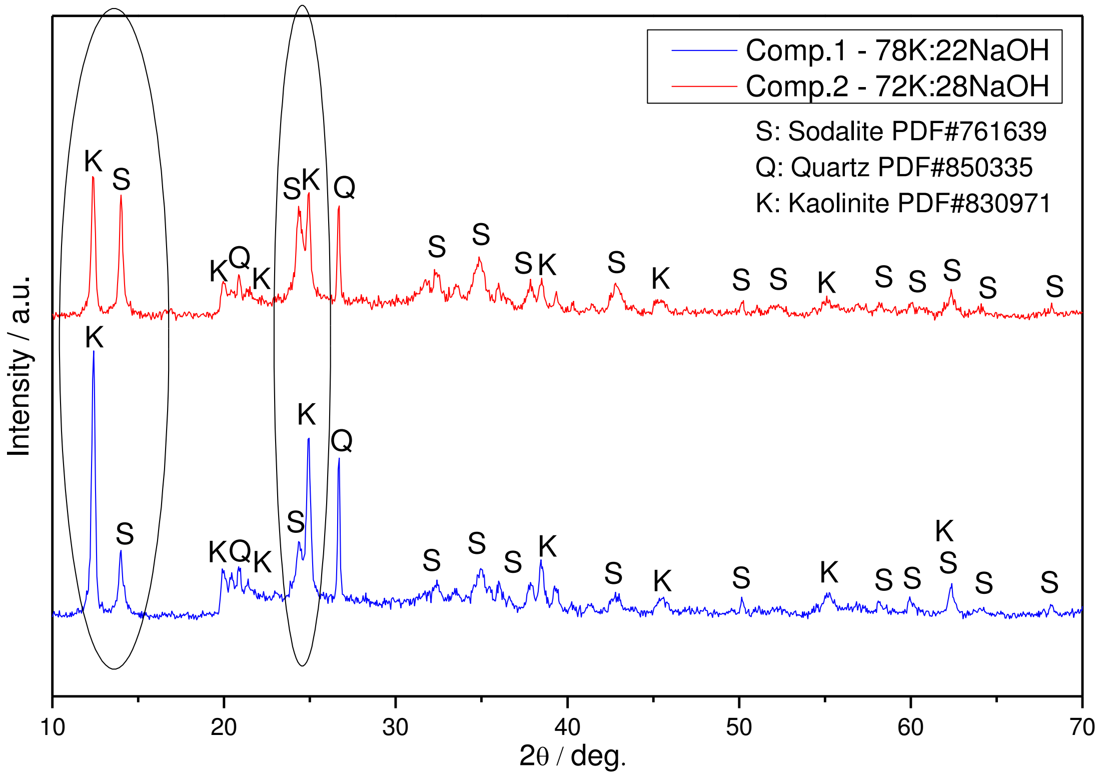


Figure 2.6 :XRD analysis of samples pressed at 20MPa 150°C for 7min

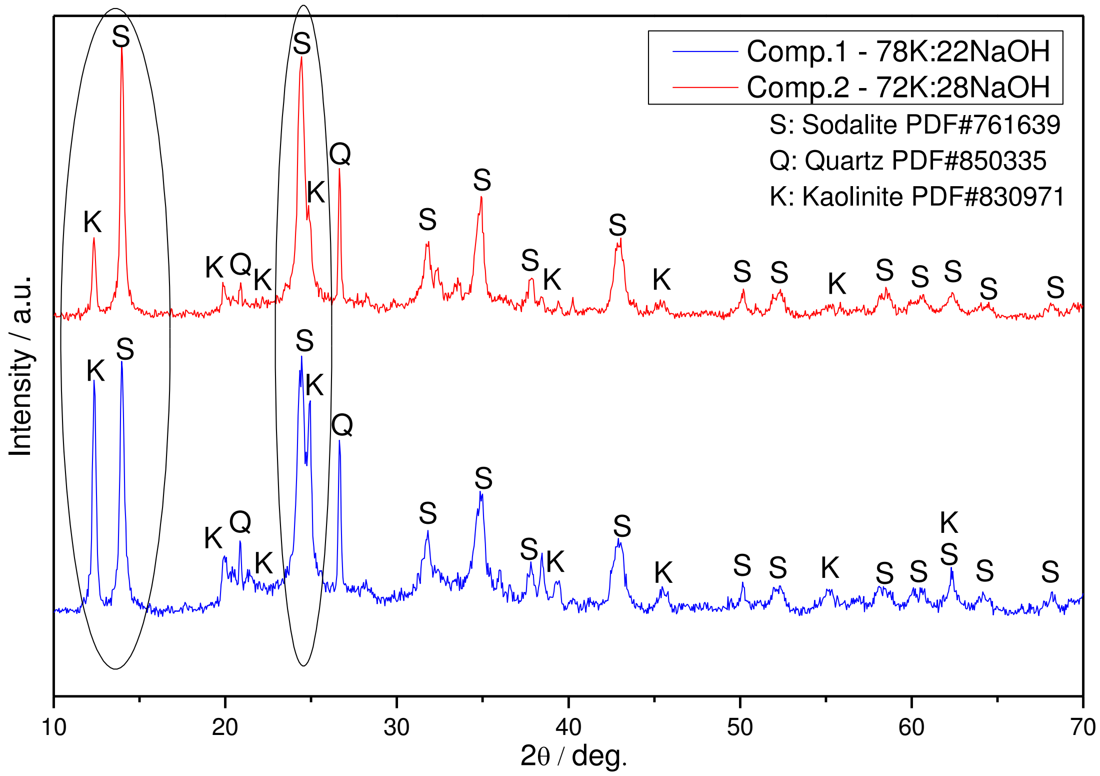


Figure 2.7: XRD analysis of samples pressed at 20MPa 150°C for 10min

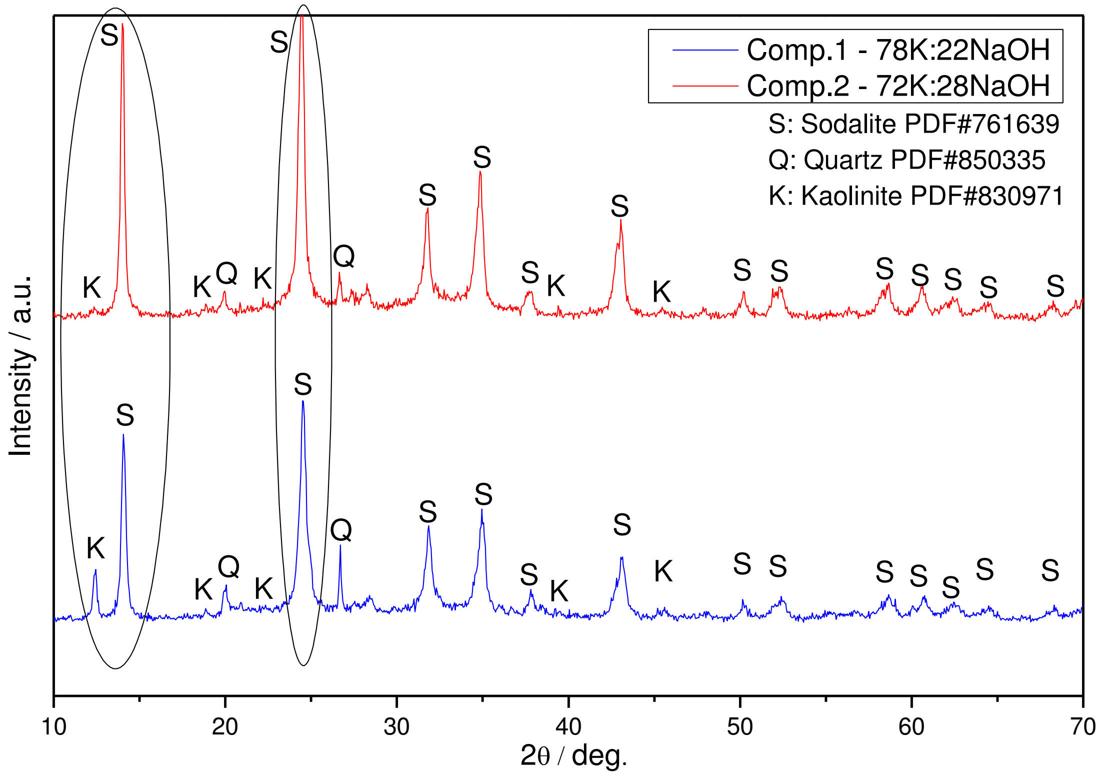


Figure 2.8: XRD analysis of samples pressed at 20MPa 150°C for 60min

With the idea to use an automatic online XRD analysis to control the reaction's conversion at industrial level, a fast and semi-quantitative method was developed. [40]

The Rietveld quantitative analysis has not been considered, because it takes a long time to carry out. So, the reaction's conversion was estimated using the ratio of the two main peaks of hydrosodalite and kaolin from the XRD analysis. The main peaks are located:

- at 24.5° for Hydrosodalite (Cukα)
- at 12.4° for Kaolin (Cukα)

In **fig. 2.9** is shown the effect of time and composition on the conversion. The standard deviation is comparable to the dimension of the dots in the graph.

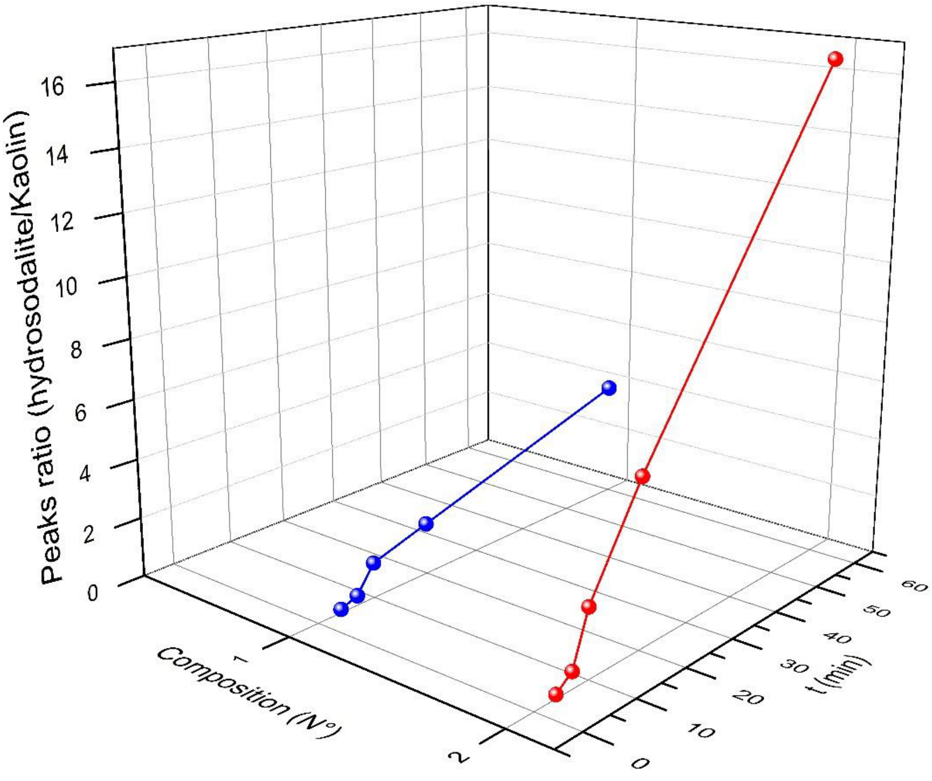


Figure 2.9: Effect of time and composition on conversion

The kinetic study showed how:

- The hydrothermal reaction probably begins after 5 minutes.
- The basic sodalite conversion increases with time.
- The composition had an effect on the kinetics of the reaction. The conversion was enhanced for the composition with the highest NaOH content.

- For a pressing time of 60min (**fig. 2.8**), kaolin was almost completely converted in basic sodalite, working with the stoichiometric composition (N°2)
- The XRD results showed the formation of basic sodalite. The reaction happened in absence of water, so it didn't proceed with first a dissolution of the kaolin structure.

The mechanism of the reaction has not investigated more, because we were interested on the production of brake pads and we found a system which didn't require to modify the technology production of phenolic based brake pads.

However, a hypothesis has been done. Working at 150°C, the pressure of 20 MPa was very high compared to the saturation pressure of water, equal to 0.5 MPa. The dry Siliface process, can be effectively considered a solid-state synthesis, so the diffusion of ion is very low. The high-pressure value probably permits the rearrangement of the structure at short range. The kaolin structure consists of one octahedral sheet and one tetrahedral sheet. The base sheet hexagonal structure of kaolin, in high temperature and pressure conditions, could behave as nucleation site for the crystallization of the hexagonal face of the sodalite cubic structure, **fig. 2.10**. It has sense to suppose that the water produced during the reaction could help the reaction giving a partial dissolution of sodium hydroxide, and so giving a real hydrothermal condition.

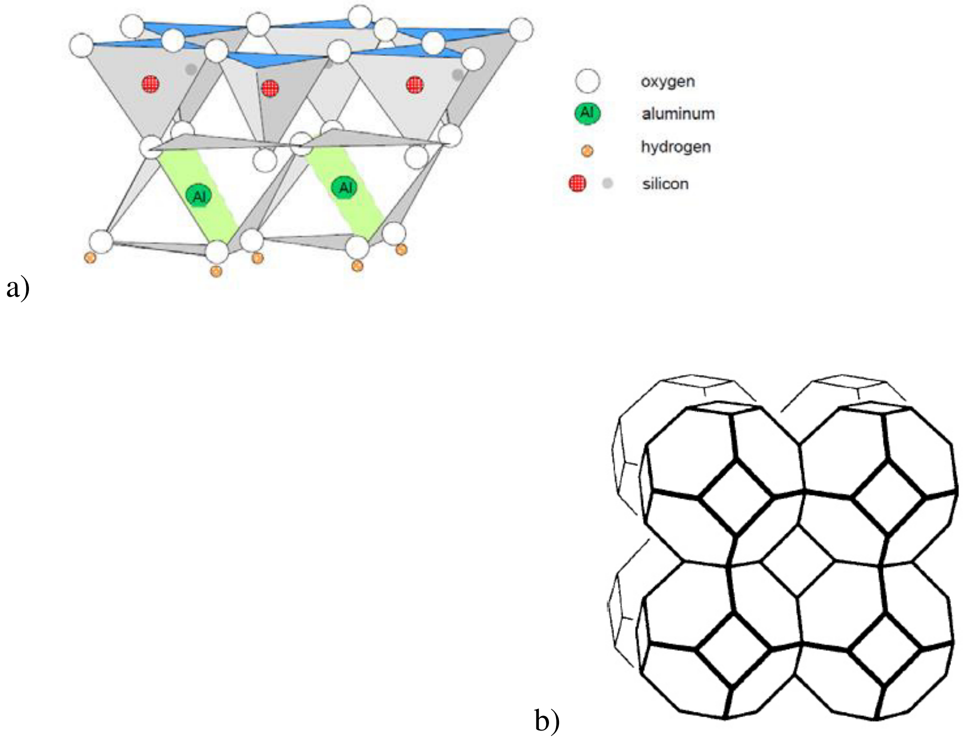


Figure 2.10: Kaolin (a) and basic sodalite(b) crystalline structures [41] [42]

For the kinetic study we did not consider the effect of the granulometry on the conversion, because due to the hygroscopicity of sodium hydroxide, it was difficult to sieve the mixed powder and to divide the different powder granulometry. And working with unreacted powder, a possible segregation of raw materials could occur, because kaolin was very fine (<10microns) so the smaller granulometry could be richer in kaolin than theorical composition.

2.3 PRODUCTION OF KAOLIN-SODIUM HYDROXIDE POWDER

During the kinetics study the mixing of kaolin with sodium hydroxide was in dry condition, using the ball milling technology, with a first step to grind the sodium hydroxide and a second step to mix the kaolin and sodium hydroxide. Considering a mix system at industrial level, the limit of the described approach was the handling of pure sodium hydroxide powder, with all the related safety problem due to the causticity of the powder.

To solve the safety problem of pure NaOH powder handling, two mixing methods were investigated: wet and dry method.

2.3.1 Wet mixing of kaolin-NaOH system

For a preliminary investigation, to find the best drying method NaOH and Kaolin were mixed in solution with a weight ratio water:NaOH = 4:1 and using a laboratory mechanical stirrer, mixing for 10 min at 1000 rpm. At the end a sticky paste was obtained. We used the composition which maximized the basic sodalite conversion. To eliminate the water, 3 different evaporation processes were used:

- Static oven
- Vented oven
- Vacuum assisted drying

The dried materials were ground by ball milling at 450 rpm for 30min.

2.3.1.1 Oven drying

Both for static oven and vented oven, the drying was conducted at 40°C for 72h. The loss in weight after the treatment showed how the water was not completely eliminated for the two system. Also, the XRD analysis in **fig. 2.11** showed that kaolin and NaOH have partially reacted giving basic sodalite. For some peak X it has not been possible to give an assignment. It meant that at 40°C the NaOH solution was able to attach the kaolin and to give the dissolution of the alumino-silicate with the formation of sialate monomers. From literature it's known that starting from 35°C kaolinite is dissolved in high molar KOH solution and transformed into zeolite products, due to the uniform distribution and availability in kaolin of the sequence Si-O-Al [43]. The result showed how it happens for NaOH solution too.

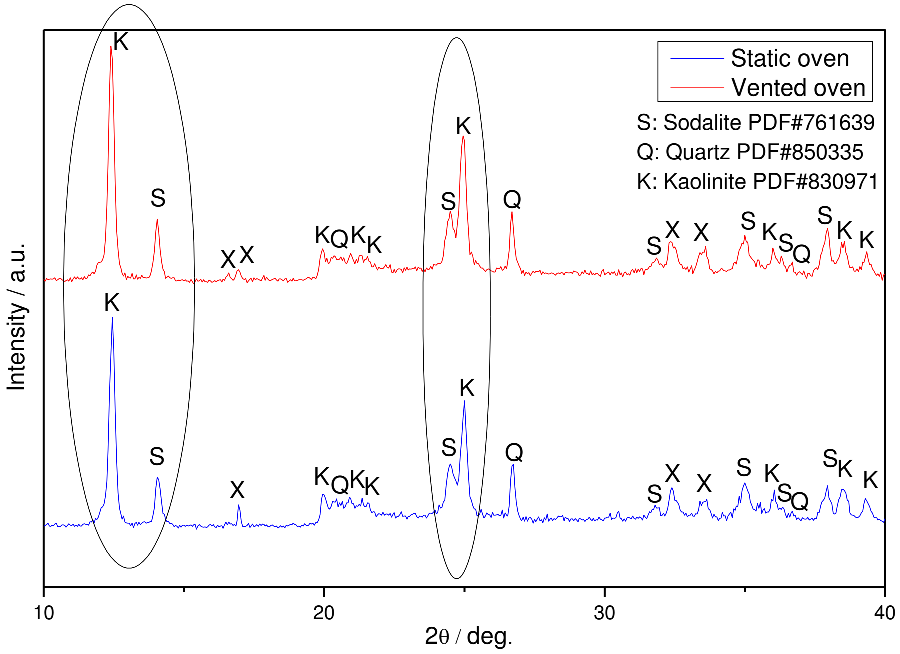


Figure 2.11: XRD analysis on oven dried kaolin-NaOH paste

To evaluate if the partially reacted powder was able to be used, the powder was pressed at 150°C and 20MPa for 10min. The densification of powder was not observed. So, it means that a partially reacted powder is not able to react to give a major conversion during a hot pressing in dry condition. Therefore, the evaporation in oven at 40°C was not suitable for this process.

2.3.1.2 Vacuum assisted drying

The vacuum drying was considered, because it permitted to dry at RT the kaolin-NaOH paste in order to prevent the reaction of the reagents. To vacuum dry the paste a Labconco Free Zone 2.5 has been used. The drying was conducted at RT for 48h and with $P < 0.1$mbar. Looking to **fig. 2.12** it's possible to observe how to remove water from a sodium hydroxide solution, the lowest pressure required is approx. 0.5cm of Hg = 6.7mbar. But working at laboratory scale the system was in static condition, so we decided to enhance the water evaporation decreasing the pressure of the vacuum dryer chamber. In particular the low-pressure value was fixed considering the slowest evaporation process, which correspond to the zone 15th of the

Water/NaOH phase diagram **fig. 2.12,** where it is required to remove the water from the solid hydrate sodium hydroxide. A time of 48h was required to remove completely the water used to mix kaolin and NaOH. In **fig. 2.13** the Labconco system and the dried material were shown.

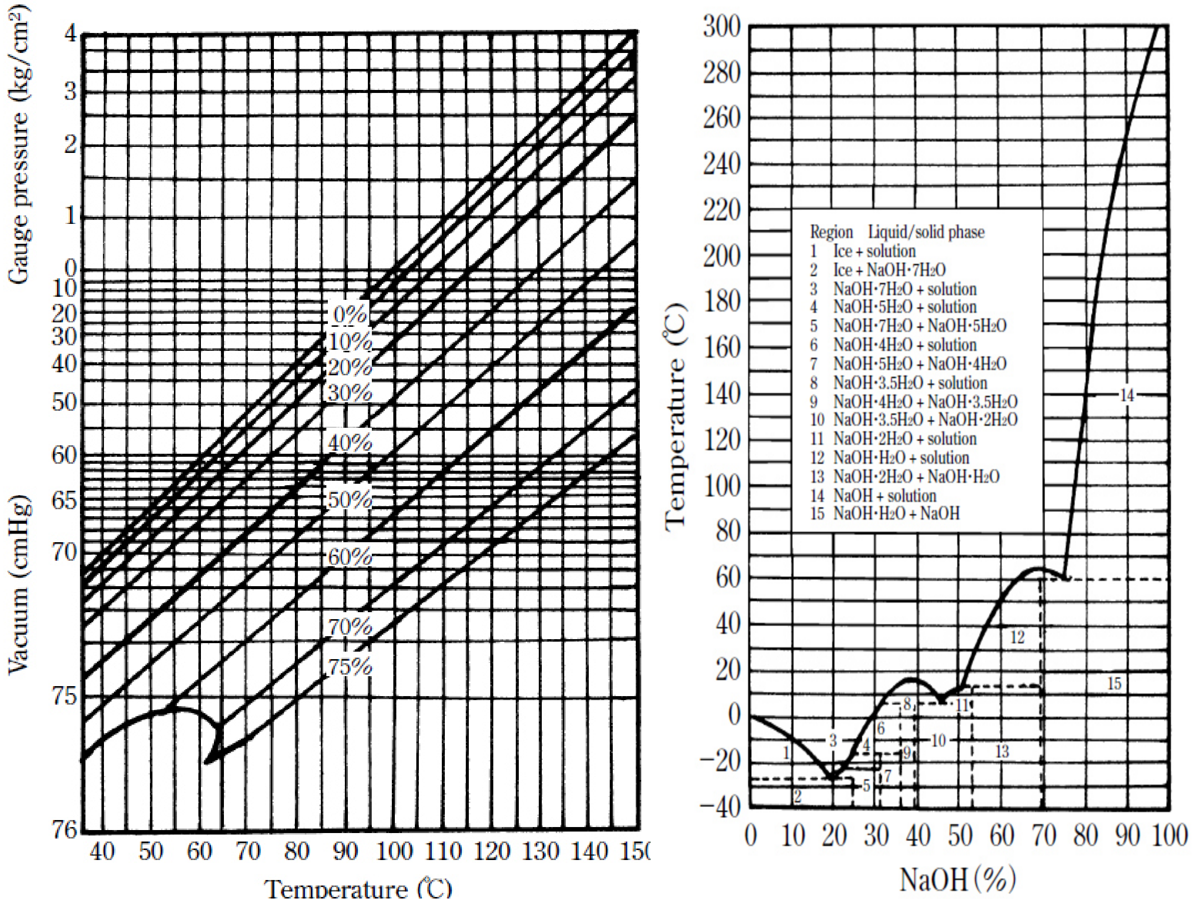


Figure 2.12: Water-NaOH phase diagrams [44]

Figure 2.13: Vacuum drying system (left) and dried material (right)

The XRD analysis showed that conducting a vacuum assisted evaporation at RT prevented the reaction between kaolin and NaOH. The dried material was then ground. It was supposed that the material was homogeneous, so in agreement with ITT Italia the powder was sieved to a granulometry smaller than 300microns to minimize the powder volatility and the surface area to reduce the hygroscopicity of the powder.

As last step on the definition of the wet mixing method, in order to decrease the drying time with the vacuum drying technology, we decided to decrease to the minimum value the amount of water. The NaOH solubility in water at 20°C is approx. 1100g/l [44], so it was decided to work with a NaOH/water weight ratio of 1:1 with a quasi-saturated solution of sodium hydroxide. With this amount of water, we did not obtain a sticky paste, but a semi-dried material, so we processed it to have the formation of humid granules of kaolin-NaOH, by the use of a Kenwood planetary mixing **fig. 2.14**.

Figure 2.14: Lab. planetary mixer (left), humid kaolin-NaOH granules (right)

On the base of the laboratory test, different industrial process have been evaluated for the wet mixing and drying of NaOH-kaolin and to have at the same time the grounding of the powder. A preliminary test in Amixon, Germany has shown which was better to work with the minimum amount of water, because during the drying, the viscosity of the kaolin-NaOH-water paste increased with the reduction in water content, due to the evaporation. At the same time the pseudoplastic behavior of the paste increased, causing problem with the mixing engine of the machine.

In Italvacuum, Italy a test based on the granulation of the kaolin-NaOH were carried out. With this test it has been observed how at industrial level was not possible to reach the pressure used for the lab studies. It caused long time for the drying major than 1 week with a considerable increasing in term of cost production.

Due to not promising results of the test and considering the intellectual property of the machine the details of the test are not reported.

2.3.2 Optimized dry mixing of kaolin-NaOH system

We still considered the dry mixing, because after the not promising results of industrial wet mixing and drying test, it has been re-evaluated the dry mixing.

To minimize the number of process phases and so the exposure time of sodium hydroxide to the air, the grounding of sodium hydroxide and the mixing phase were done at the same time. Using the ball milling technology NaOH and kaolin were mixed and ground together in one-step at 450 rpm for 30 min.

Production method	***Hydrosodalite conversion: peak ratio (S/K)***
Not optimized dry mixing	2.3 ± 0.2
Optimized dry mixing	3.3 ± 0.2
Wet mixing + RT vacuum drying	3.2 ± 0.3

Table 2.1: Effect of mixing method on hydrosodalite conversion

To compare the effect of the wet and dry mixing on the hydrosodalite synthesis, the samples obtained from the wet method with vacuum assisted evaporation and from the optimized dry method were pressed at 20 MPa and 150°C for 10 min. The results described in terms of basic sodalite conversion are reported in **table 2.1.**

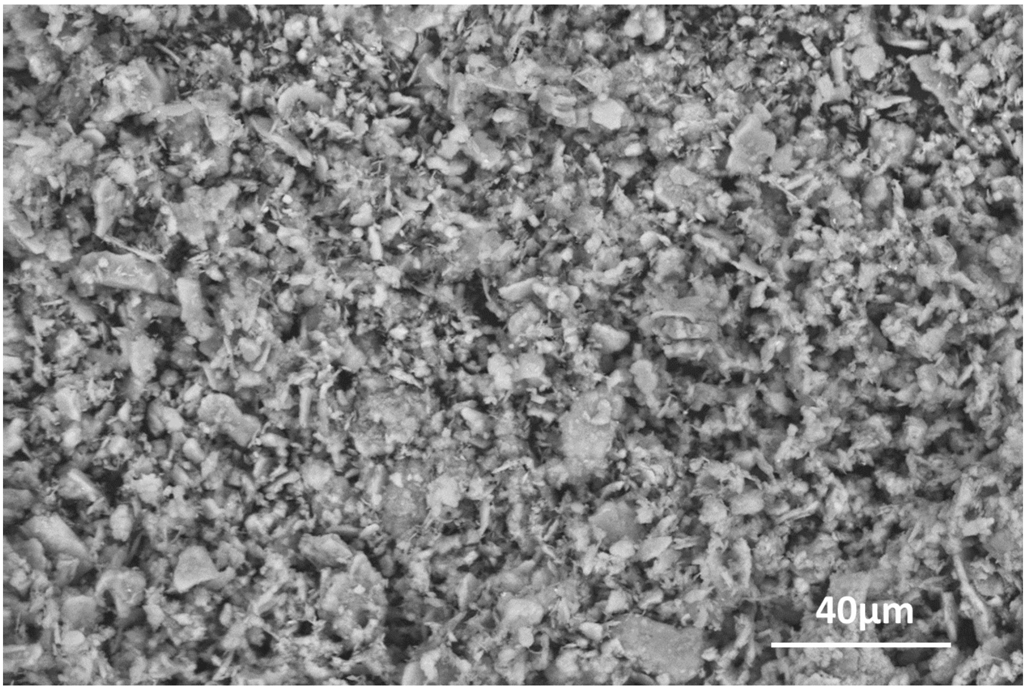


Figure 2.15: SEM analysis of powder from optimized dry mixing method

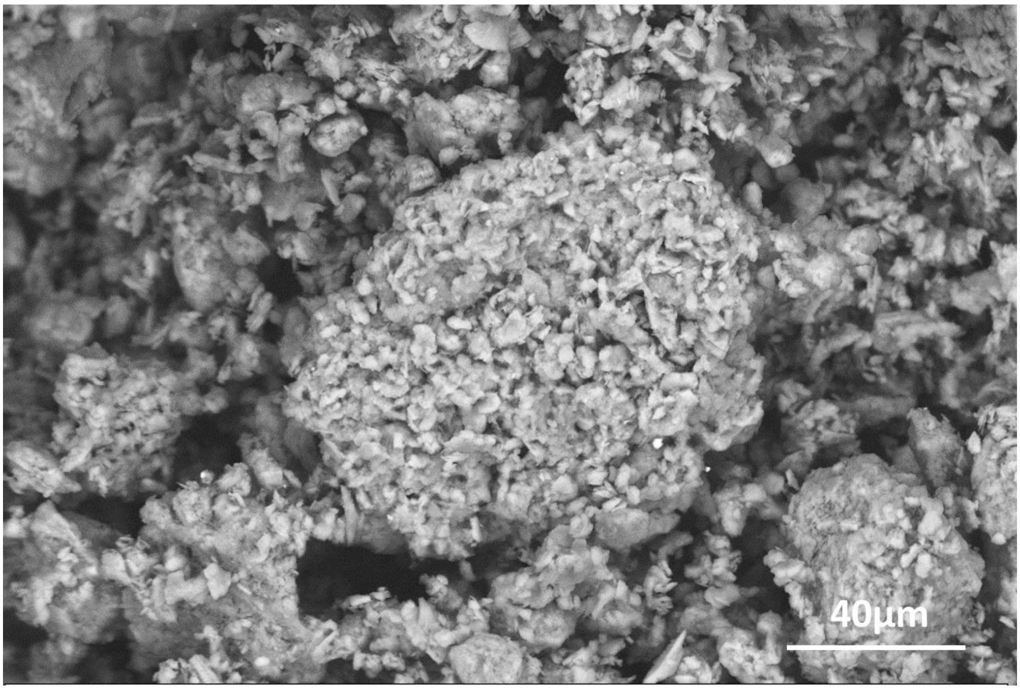


Figure 2.16: SEM analysis of powder from wet mixing method

Considering the comparison of conversion and powder granulometry **fig. 2.15 and 2.16**, in function of the mixing process, it was possible to observe how the optimized dry mixing process possessed a reactivity similar to the wet mixing process, but with a smaller granulometry. Both the methods improved the conversion compared with the not optimized dry mixing.

With the wet mixing process the sodium hydroxide crystalized on the kaolin particles during the drying, so it permitted to increase the interaction of the raw materials, even working with powder below 300microns and so, bigger than the powder obtained with the optimized dry mixing method.

An industrial test for the mixing of NaOH and kaolin was done in ISTEC, Italy using a jar rotator sealed system **fig. 2.17**, to prevent the absorption of humidity. The jar rotator machine worked at lower energy compared to ball milling, but a good grounding quality could be obtained working with long mixing time.

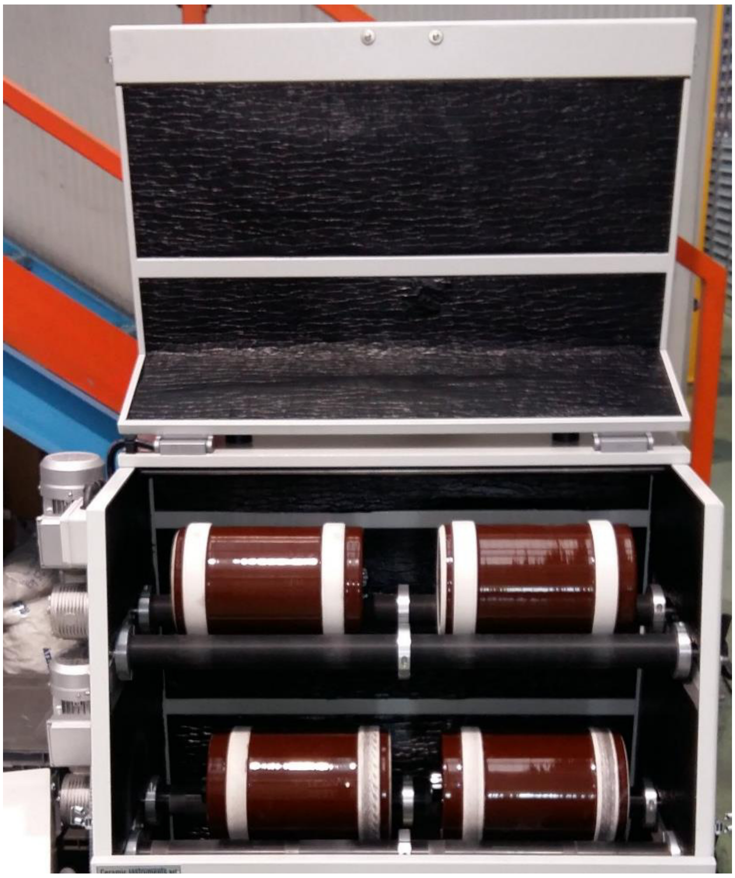


Figure 2.17: Jar rotator system

Thanks to the ability to control the conversion of the hydrothermal reaction, to have the formation of basic sodalite and defined an appropriate mixing method, we were able to produce an amount of geopolymer binder which permitted to develop a brake pad formulation based on the kaolin-NaOH system.

2.4 DEVELOPMENT OF BRAKE PADS FORMULATION

To develop an optimized friction formulation based on the kaolin-NaOH system, the study started from an ITT Italia reference formulation for the type of brake pad selected, in relation with the "Segment B" vehicle chosen for the project. The production of brake pads has been done with the hot molding machine of ITT Italia and it was not done any test of brake pads production at the university of Padova.

The Struers Prontopress-2 machine worked with a ramp heating step, so it took some minutes to reach the temperature and it didn't permit to use degassing step as normally required during the production of brake pads, to remove the gas generated from the reaction.

For the starting formulation the phenolic resin was substituted with kaolin-NaOH binder, so a mix of the two binders was not considered as solution. During the project different modifications to the formulation were done, in function of the friction properties and of the conversion of the kaolin-NaOH into basic sodalite, in the brake pad system. At the end of the project 56 formulations based on kaolin-NaOH system were investigated.

On the present thesis the main aspect will be reported. The details of the formulation cannot be reported because the property of the results is of ITT Italia. A general description of the formulation is reported in **table 2.2**.

Constituents	***% Weight***
Kaolin-NaOH	20-50
Lubricant 1	5-10
Lubricant 2	5-10
Lubricant 3	5-10
Filler 1	2- 7
Filler 2	2 – 7
Metallic fibers	10-20
Organic	5-10

Table 2.2: General description of developed friction formulation

The brake pad composition was defined taking in account that the geopolymer matrix has a hardness comparable to the medium abrasives normally used in brake pads and considering that the sialate-based geopolymers were used as matrix for bricks and ceramic. For this reason, in geopolymer based brake pads it was decided to don't use any abrasive materials. So, we developed a formulation based on a geopolymer matrix, some lubricants as graphite to stabilize the wear, fillers as vermiculite to reduce the cost and metallic fibers as steel to increase the resistance and to have a good thermal conductivity. As discussed in the introduction and background, the friction formulation did not contain asbestos and copper.

The main aspect found for the production of brake pads were:

1. The production of friction formulation was done adding the kaolin-NaOH binder as last ingredient in the mixer chamber, and to seal the mixer to prevent the humidity absorption by the sodium hydroxide. In fact, to have cracks free brake pads, the humidity of the friction material mix (at the end of all mixing steps) had to be lower than 1%wt. This value was the same of phenolic based brake pads.
2. We produced brake pads based on both the compositions investigated during the kinetics studies of the geopolymer system.
3. Pressure and temperature were fixed at 150°C and 20MPa.
4. The ITT warm pressing machine worked with a hot mold, so a heating ramp was not required. For this reason, the time production of brake pad was 3 min lower than the time considered with the Struers lab machine.
5. Similarly to phenolic based brake pads, a degassing step had to be used to eliminate the byproduct produced from the cross-linking reaction. In case of geopolymer the byproduct was water. It confirmed the fact that the geopolymer components produced with the warm pressing machine contained cracks at the end of the molding step.
6. The presence of sodium hydroxide gave problems in terms of stability at the air of the friction formulation, with consequences on the reproducibility of brake pads production. To prevent the humidity absorption, the formulation was stored in sealed vessel, however during the weighing the humidity was absorbed.

   Considering this problem, it has been observed how it was possible to produce a major amount of brake pads with an acceptable quality, so without cracks, for the friction formulation based on the kaolin-NaOH composition with the lowest content of sodium hydroxide.

In **fig. 2.18** it’s shown some brake pads produced with the optimal pressing conditions. No cracks were observed and a good adhesion with the UL was obtained. In **fig. 2.19** it is also interesting to observe how due to the geometry of the brake pads used for the project, it has been possible to conduct the XRD analysis directly on the pads surface. The XRD data analysis collected from the surface and the bulk of a brake pad were similar, therefore the XRD analysis has been conducted only on the surface of the pads., having an easier and non-destructive analysis method.

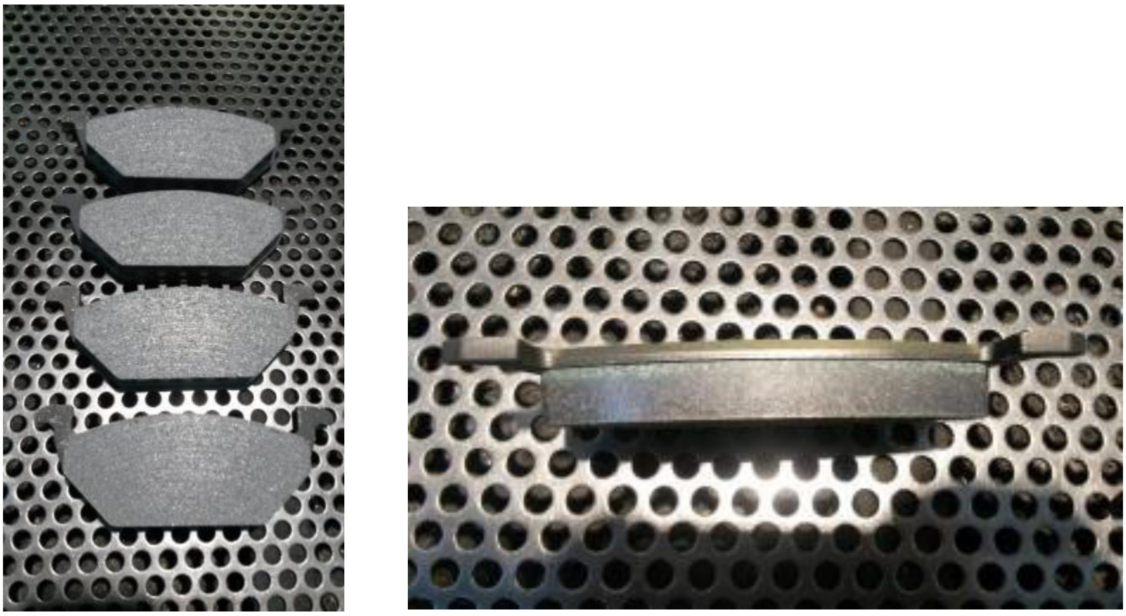


Figure 2.18: Brake pads produced with the optimal pressing conditions

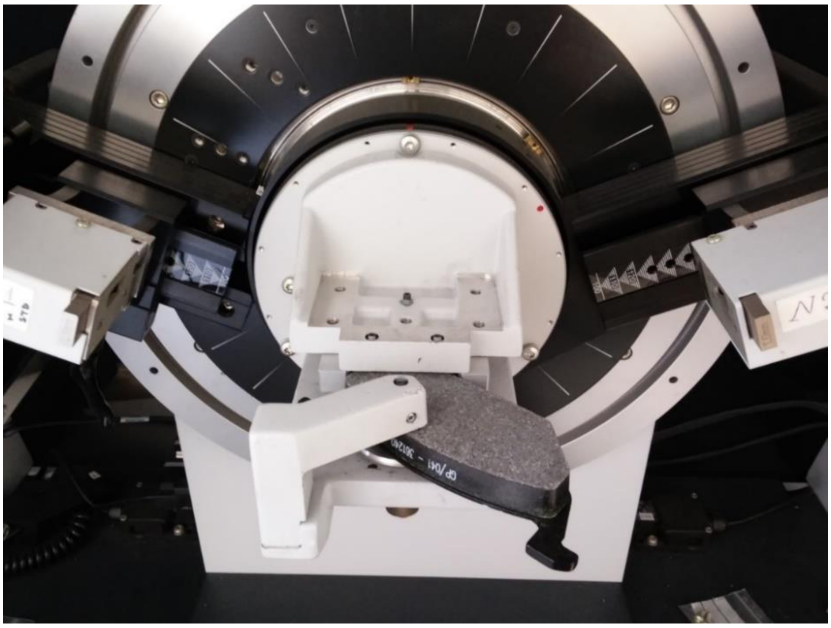


Figure 2.19: Example of a brake pad XRD analysis

2.4.1 Friction formulation optimization: basic sodalite conversion

We won't discuss the value of hardness, density and mechanical properties of the brake pads, because they depend on the friction formulation and on the content of each ingredient. But cannot reporting the friction formulation, it's not possible to do comparison evaluation. So the only effect associated to the geopolymer matrix will be discussed.

On the first brake pad formulation which exhibited promising physical properties (hardness and porosity) the XRD analysis was done. In **fig. 2.20** is reported the result for a brake pad pressed for 7min and based on a geopolymer with a ratio kaolin-NaOH = 1:2. For the first friction formulations we preferred to work with the less hygroscopic geopolymer composition.

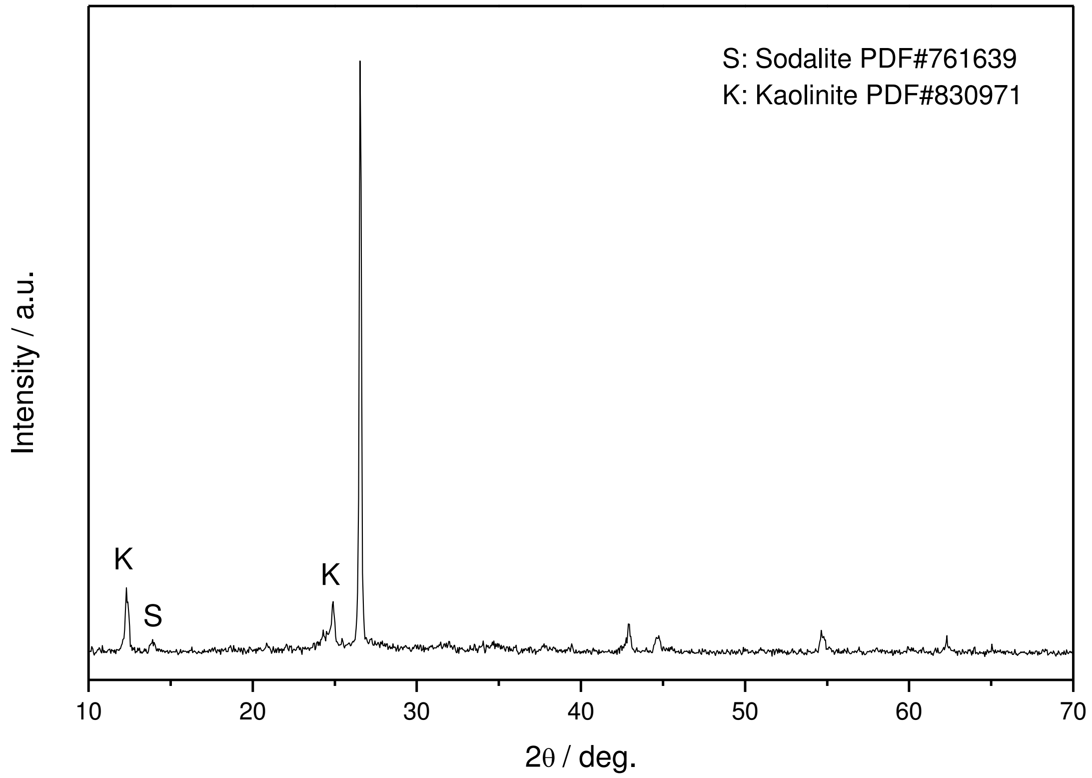


Figure 2.20: XRD pattern of a non-optimized friction formulation: lower conversion than pure matrix

We found that the basic sodalite conversion on the brake pad system equal to 0.26 was much lower than the conversion of the pure geopolymer system which was 0.88.

Similarly to the kinetics studies, to define the conditions which enhanced the basic sodalite conversion on the brake pad system, the effect of time, geopolymer content and composition were evaluated.

The results indicated that:

- Increasing the pressing time and the NaOH content, an effect on the basic sodalite conversion was not observed.
- The kaolin residual signal was proportional to the theorical geopolymer content and to the kaolin content in the geopolymer's composition, confirming the absence of the reaction independently on the geopolymer content

So in the brake pad formulation, there was an interaction of the kaolin-NaOH system with the other raw materials which were present in the brake pad. To evaluate the type of interaction which occurred in the system, a study of each raw material effect on the hydrosodalite synthesis has been carried out. It was evaluated not only the conversion of the basic sodalite, but also the effect of the single raw material on the friction properties of pads.

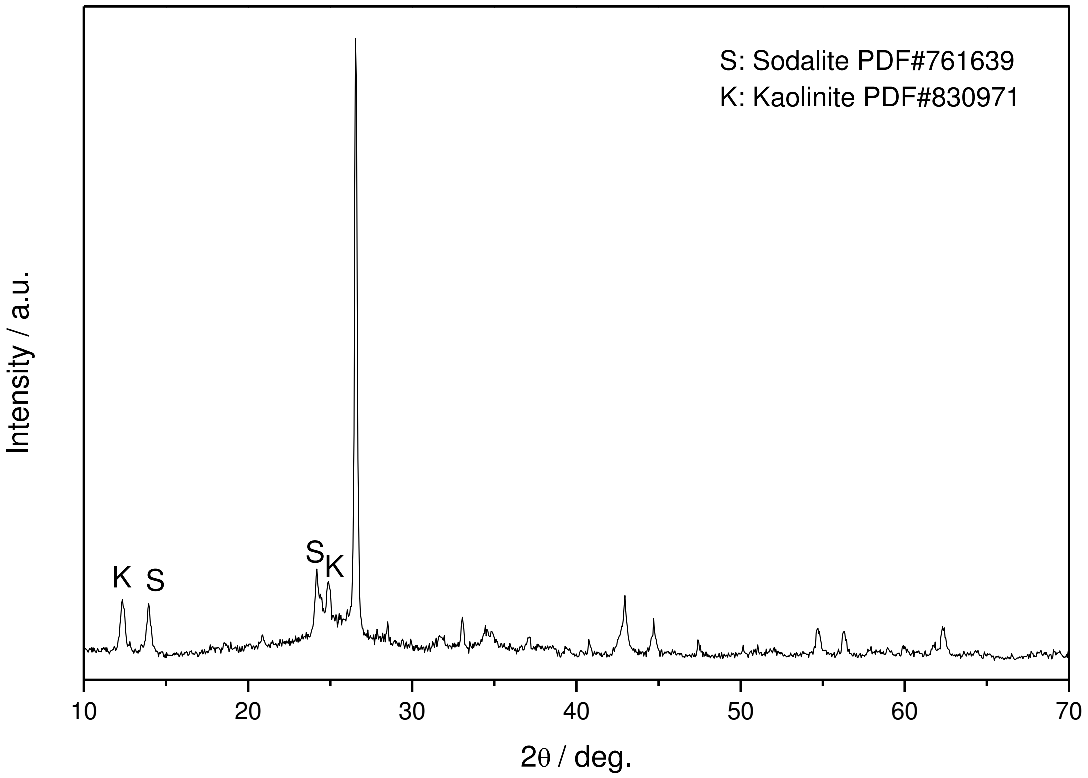


Figure 2.21: XRD pattern of an optimized friction formulation: conversion similar to pure matrix

Removing the tin sulfide, (a raw material normally used as lubricant in the brake formulation) a benefit effect was observed on friction properties and in particular on the basic sodalite conversion. The XRD analysis on a pad of the optimized formulation is shown in **fig 2.21**. The pad was based on the same matrix type (1 kaolin: 2 NaOH) and pressed for 7min at 150°C and 20MPa. The conversion was 0.81. To evaluate the improvement in term of reactivity of the optimized friction formulation the XRD analysis was carried out on the same formulation but using as matrix the geopolymer with the highest Na content (3Kaolin: 8 NaOH). The conversion was 2.17 and the result is shown in **fig.2.22**.

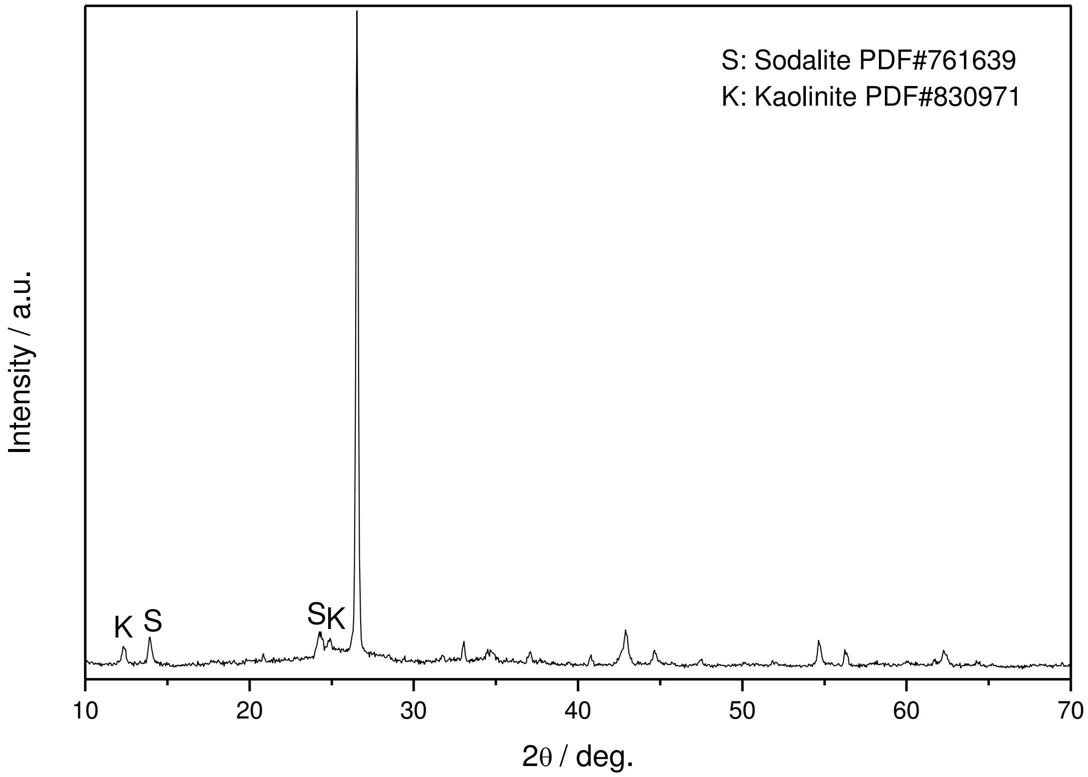


Figure 2.22: XRD pattern of an optimized friction formulation with the highest NaOH content: conversion similar to pure matrix

For the optimized composition where tin sulfide was removed, it was possible to observe a conversion of kaolin-NaOH into hydrosodalite that was the same of the geopolymer system without any filler.

The interaction of tin sulfide with the synthesis of basic sodalite has not been investigated more, but a hypothesis has been done.

A secondary hydrothermal synthesis of a lapis lazuli mineral $Na_8(S_2)(Al_6Si_6O_{24})$ [45] could be activated during the pressing, due to the contemporary presence of sodium and sulfur in the formulation. The lapis lazuli is a mineral of the same class of hydrosodalite. The presence of two competitive reactions, which could decrease the conversion of kaolin-NaOH into basic sodalite, it could explain the low degree of conversion. Peaks of lapis lazuli were not found on the XRD pattern, but it could be that the lapis lazuli's reactivity was slower than the sodalite synthesis. However, the sulfur in the system could reduce the sodium available for the sodalite synthesis. In order to maintain the friction behavior, the tin sulfide was substituted by iron sulfide. It has not been observed an interaction of iron sulfide with the kaolin-NaOH system.

2.4.2 AK-master and TL110 characterization results

An interesting comparison between the optimized and non-optimized friction formulation could be done for the AKM Master analysis.

Despite of the absence of basic sodalite formation during the hot-pressing process for the non-optimized formulation, the brake pads had good physical properties similar to the organic based brake pads. In **fig. 2.23** and **2.24** the AK Master behavior and AKM - TL110 wear of a commercial organic-based friction formulation like an aftermarket, it is compared with the optimized and non-optimized geopolymer based formulation.

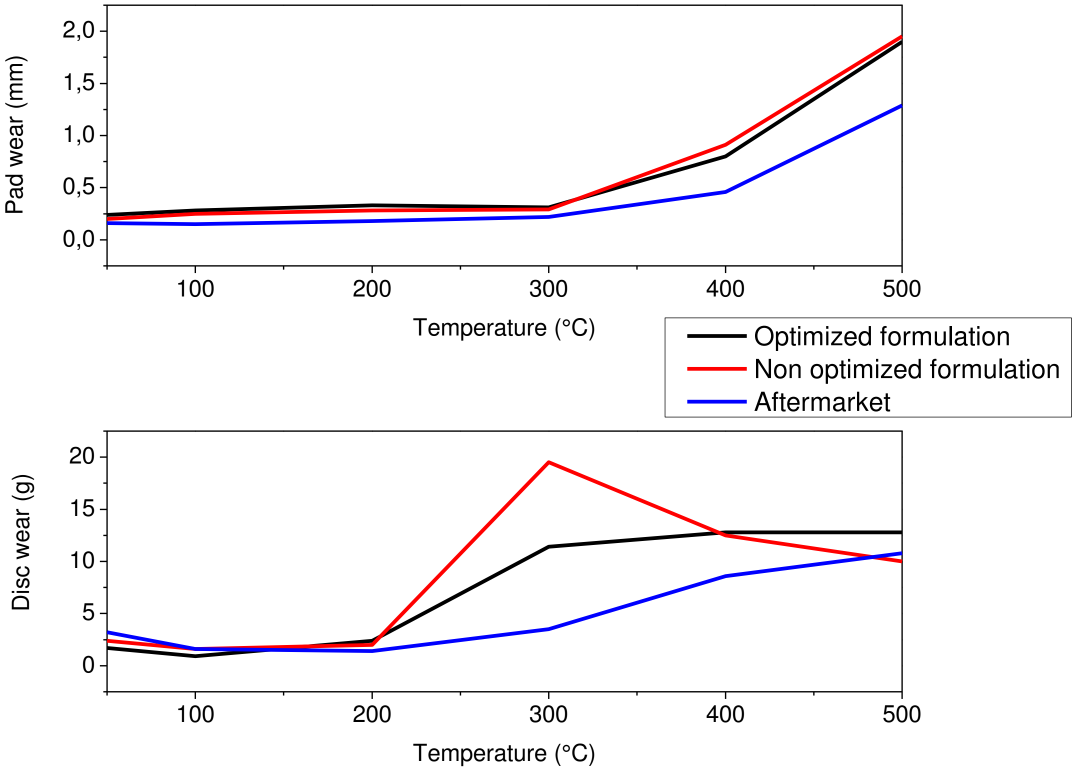


Figure 2.23: AKM - TL110 test: pad and disc wear compared for the different formulations

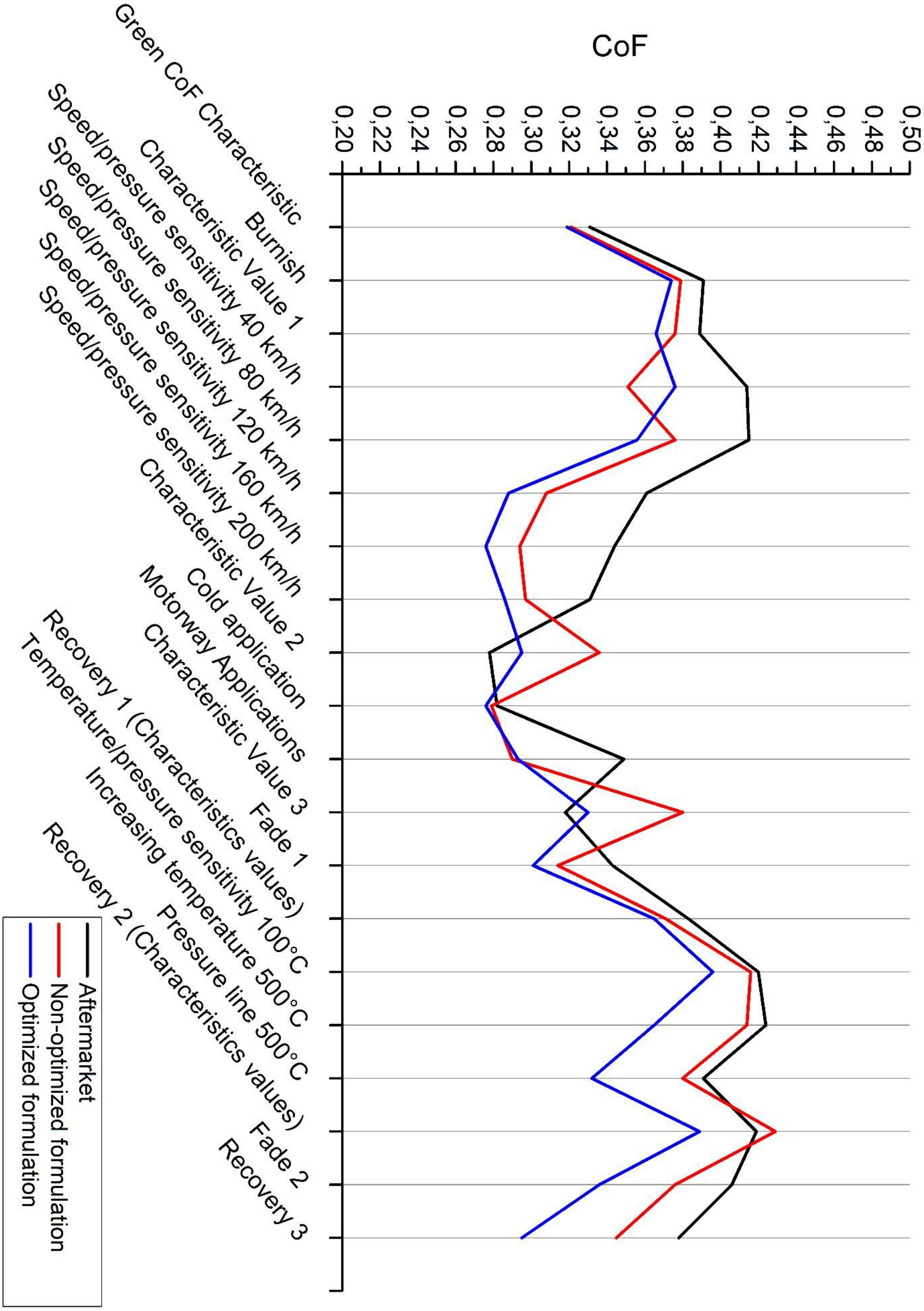


Figure 2.24: AKM test: Comparison of the behavior in terms of CoF for the different formulations

Specifically, the AK Master results showed how the friction behavior of the non-optimized geopolymer formulation was comparable with the optimized, and the aftermarket formulations. Moreover the geopolymer based formulation had a better speed/pressure sensitivity compared with the phenolic based, and it is an index of a good stability of the material. The medium value of fade was good, but it was not constant, and it could be associated to the other raw materials of the formulation, because the matrix were inorganic so less sensitive to high temperature than the phenolic resin. The same trend was observed for the wear results from the TL-110 where for the pad wear no difference were observed between the different formulation. The non-optimized formulation showed a peak at 300°C for the disc wear, but it became lower than aftermarket for higher temperature.

On pads post AKM test, **fig. 2.25**, the XRD analysis showed the formation of nepheline, the high temperature crystalline anhydrous form of sodalite. Nepheline is a natural medium abrasive used in brake pads. It suggested that temperatures higher than 850°C-900°C were reached on the surface of the brake pad during the AKM test. So, the formation of nepheline could explain the good friction behavior of the pads, despite of the absence of basic sodalite formation. It means that the low degree of conversion permitted to have the formation of a partial 3D network, which permitted to have the bonding of the friction formulation.

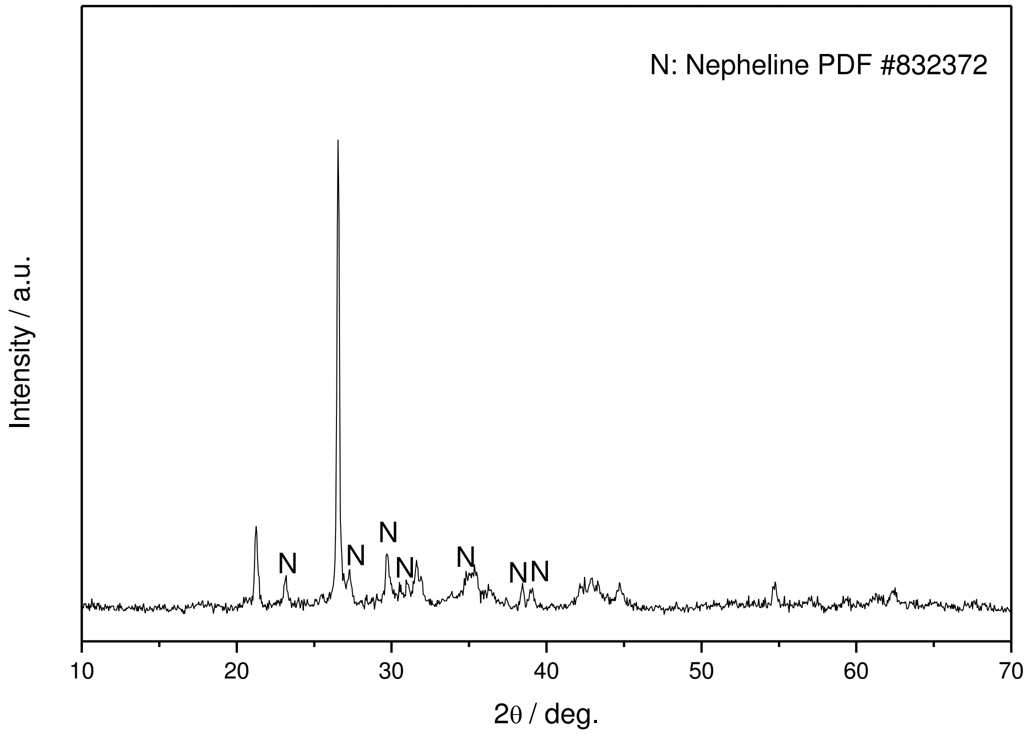


Figure 2.25: XRD analysis on a geopolymer based brake pad after AKM test

In relation with the high temperature reached during the AKM test, a secondary confirm was deduced from the XRD analysis conducted on the pad after test and with a grinding of the surface to remove a 2mm thickness, **fig. 2.26**. Due to the absence of kaolin and nepheline signal in the XRD pattern, it was possible to estimate a maximum temperature in the range of 600-800°C at 2mm from the pads surface.

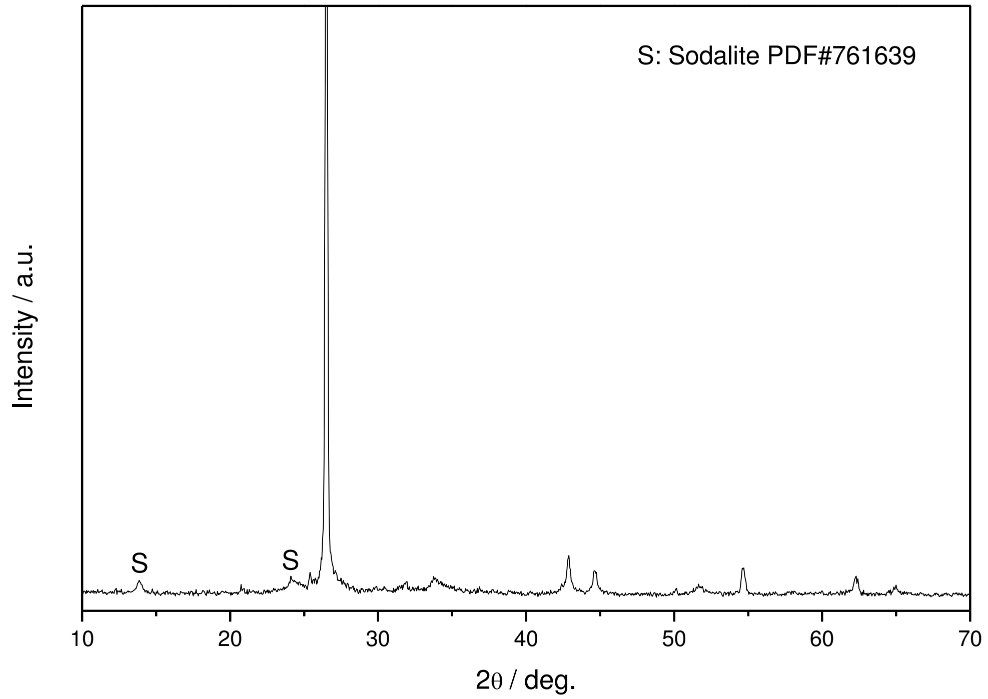


Figure 2.26: XRD analysis of a ground pad after the AKM test

2.4.3 Wolverine test results

The results of the Wolverine test showed a big problem related to the low degree of conversion observed for the non-optimized formulation. However, the same problem was most important for the optimized formulation, when a pressing time in the order of 3-4 min were considered. In fact a pressing time of 3-4 min is the typical value considered for the production of brake pads, and longer time cause a decreasing in productivity.

It is important to consider the safety requirement of the Wolverine test. This test was developed to evaluate the friction material resistance to high temperature braking phenomena. The normative required to evaluate different temperature for the test and the maximum temperature value is 600°C. And the problem was found conducting the test at 600°C.

In **fig. 2.27** is reported the graph of the test conducted on a brake pad produced at 150°C and with a pressing time of *4min*. The geopolymer matrix composition was 2NaOH:1Kaolin. In **fig. 2.28** is shown the aspect of the pads at the end of the Wolverine test. During the test at 600°C a loss of 40% in terms of CoF was measured. At the same time the pad at the end of the test showed the formation of big cracks on the friction materials.

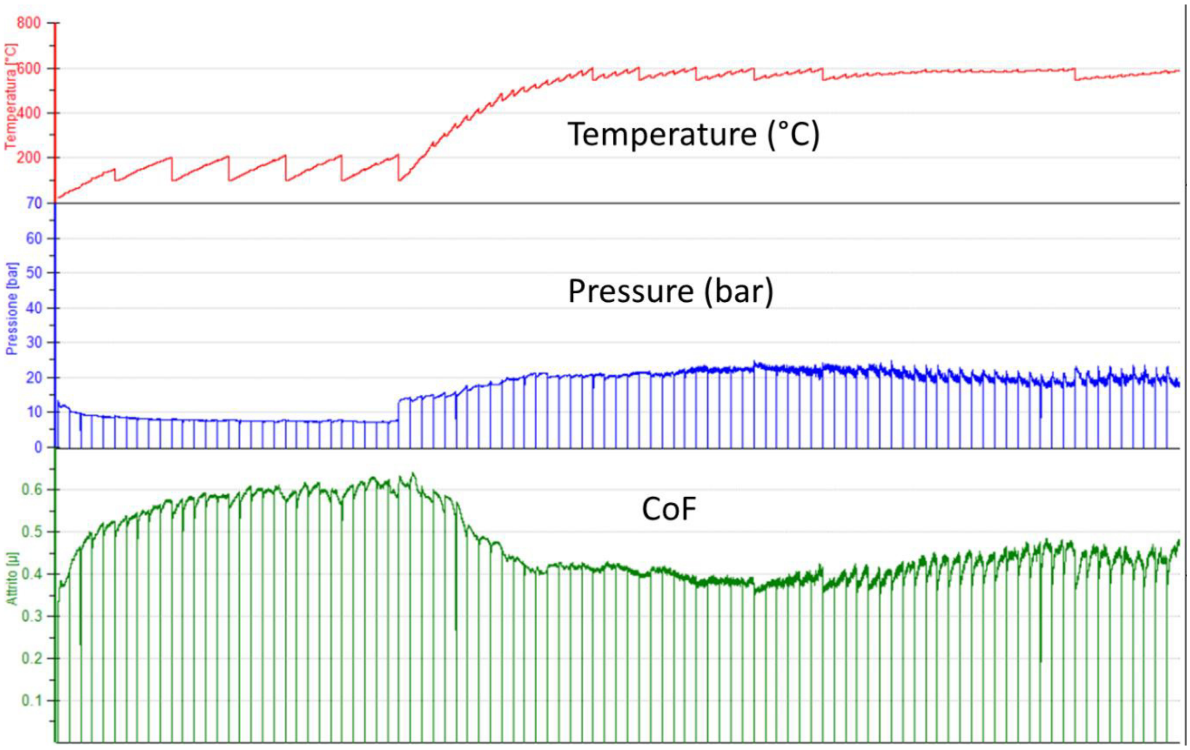


Figure 2.27: Wolverine report test for a pad with a high residual kaolin amount

Figure 2.28: Brake pad at the end of the Wolverine test: formation of big cracks

With this type of results the pad and the friction material failed the Wolverine test. To understand the reason of the cracks and the loss in term of CoF during the test, we have to consider the degree of conversion of the kaolin-NaOH system during the production of the brake pad. The degree of conversion was quite similar to the conversion evaluated by the XRD analysis in **fig. 2.21**.

The reason of the failed Wolverine test was related to the high amount of unreacted kaolin present in the friction material at the end of the production step. The kaolin decomposed by dehydroxylation at a temperature in the order of 500-550°C. In **fig. 2.29** is reported the TGA analysis on the kaolin used for the production of brake pads. It could be observed that at 500°C a loss in weight of 12%wt was observed, due to the elimination of the water from the crystalline structure of kaolin.

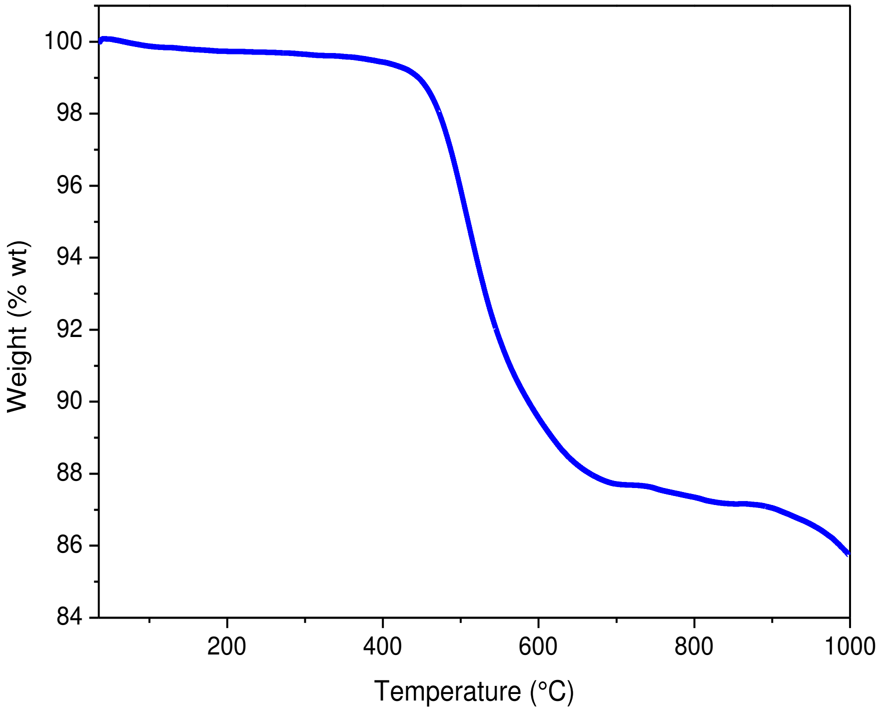


Figure 2.29: TGA analysis of the kaolin used to produce the geopolymer based brake pads

It meant that if a high amount of kaolin was still present in the pad, during the Wolverine test at 600°C a considerable amount of water was released in form of steam. The steam produced an internal pressure in the friction material, which caused the damage observed as cracks and so the loss in friction properties.

In order to solve the problems found for the Wolverine test, a low residual amount of kaolin has to be present in the friction material at the end of the hot molding phase. So to have a low residual amount of kaolin, the geopolymer composition with the highest NaOH content was the best candidate, because as described in the kinetic studies, an increasing of the NaOH content permitted to enhance the conversion of the reaction. In **fig. 2.30** is reported the Wolverine behavior of a pad produced with a pressing time of *7min* and based on the geopolymer matrix having the ratio 8NaOH:3Kaolin. The degree of conversion was quite similar to the conversion evaluated by the XRD analysis in **fig. 2.22**. With these conditions it has been possible to have a pad/friction material able to pass the Wolverine test.

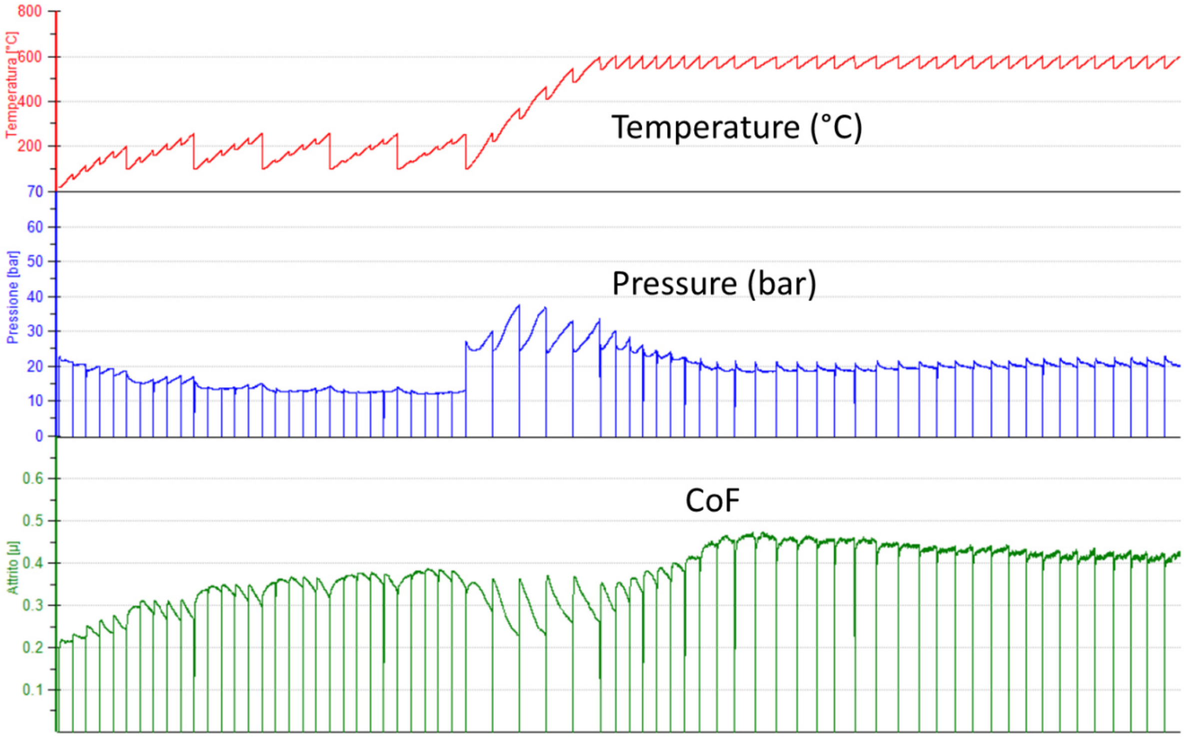


Figure 2.30: Wolverine report test for a pad with a low residual kaolin amount

The Wolverine report showed a stable CoF during the test, without the loss in properties observed for the formulation with the lower degree of conversion for the geopolymer matrix.

Figure 2.31: Brake pad with a low residual kaolin content. The pad passed the Wolverine test

At the end in **fig. 2.31** the aspect of the pad after the Wolverine test. No cracks were detected, confirming the effect of the residual kaolin on high temperature resistance of Kaolin-NaOH based friction formulation.

3-BRAKE PADS BASED ON COLD SINTERING OF GEOPOLYMER POWDER

Partially published in:
Sin A, Vannucci F, Colombo P, Conte A.: Method for manufacturing a friction material, in particular for manufacturing brake pads, and associated brake pad,
IT Patent Application 102018000008182, filed 2018-08-24

To find a more industrially viable method than kaolin-NaOH system, a new approach was considered and developed at the same with the previous, from the first year of the project. Starting from a geopolymer composition that is obtained via a conventional solution method, the produced material was ground and the powder was pressed to achieve a "re-agglomeration".

3.1 POLY(SIALATE-POLYSILOXO) GEOPOLYMERS SYSTEM

With the kaolin-NaOH geopolymer composition we found a geopolymer system able to react in absence of water and using the usual brake pads production conditions.

However, the common geopolymer technology was based on the dissolution of an alumino-silicate source in an alkali silicate solution, which behaves as alkaline activating system.

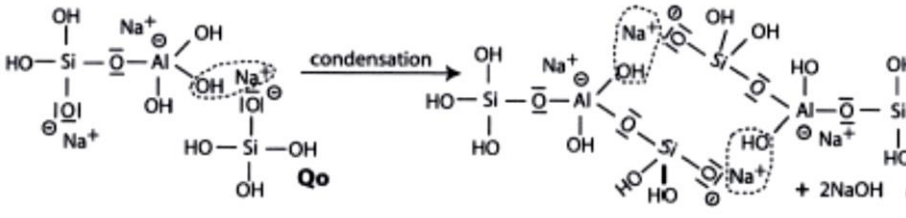
So, to use a "normal" geopolymer as binder for brake pads, but without any modification on the process production of pads, we had to adapt a water based geopolymer to work in dry condition. For the kaolin-NaOH system we removed the water, but for a common geopolymer composition we had to work on the chemistry of the geopolymer.

For a sodium-based geopolymer the dissolution of alumino-silicate to give the sialate monomers proceeded as shown in §2.1. From the step 6 in function of the Si/Al ratio different types of structure can be formed [27], due to different condensation mechanism between the sialate (created from the alumino-silicate) and the siloxonate species of the silicate solution. From "J. Davidovits, Geopolymer - Chemistry and applications 2011" [27].

"*For Si:Al=2 the ideal geopolymer structure is the Na-poly(sialate-siloxo) and the sequence is (-Si-O-Al-O-Si-O).*

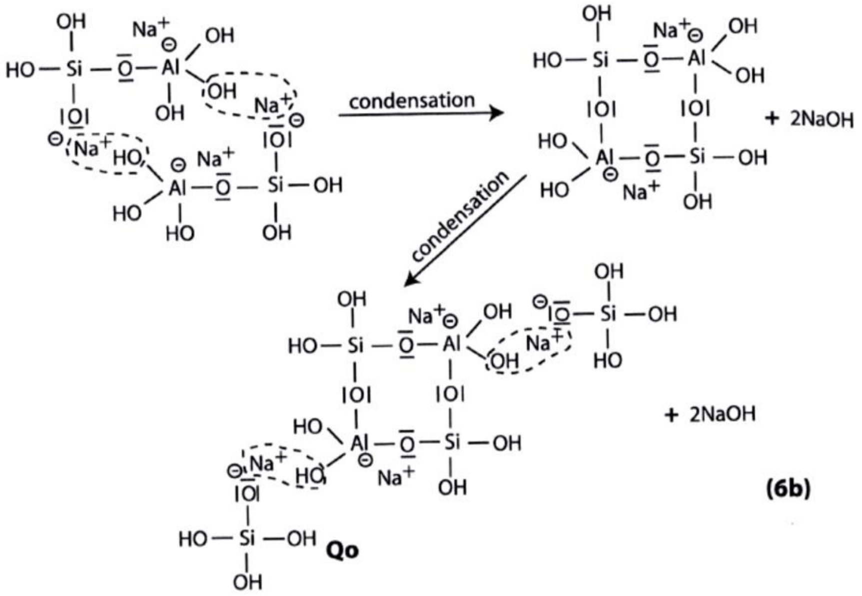
Step 6a: *show the condensation between one ortho-siloxonate Qo and one ortho-sialate molecule, reactive groups Si-ONa and aluminum hydroxyl OH-Al-, with the formation of ortho-*

sialate-siloxo linear structure which then condense into branched quadratic structure di-(sialate-siloxo).



(6a)

Step 6b: *condensation between two ortho-sialate molecules into quadratic di-sialate. Then, further condensation of one quadratic di-sialate with two ortho-siloxonate, Qo, molecules into the same branched quadratic structure di-(sialate-siloxo), as in step 6a.*



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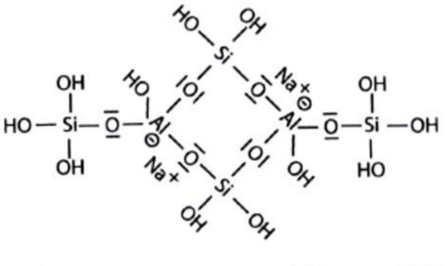

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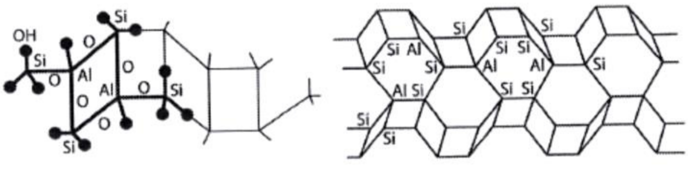
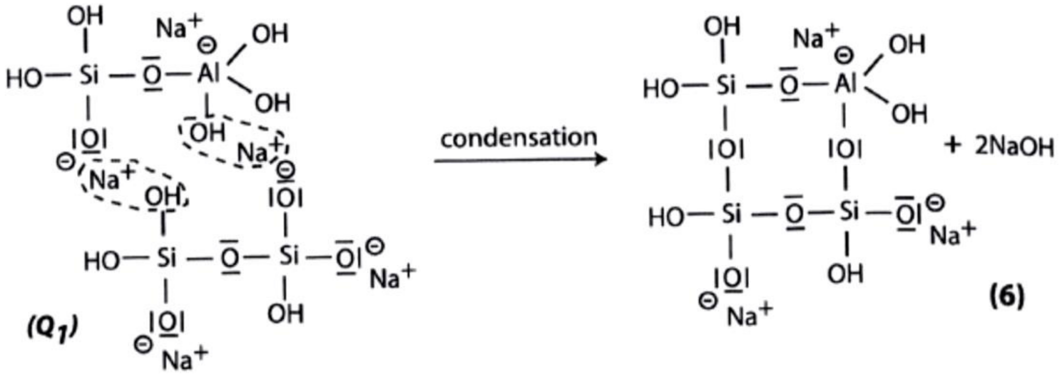


Na-Poly(sialate-siloxo)
Phillipsite framework

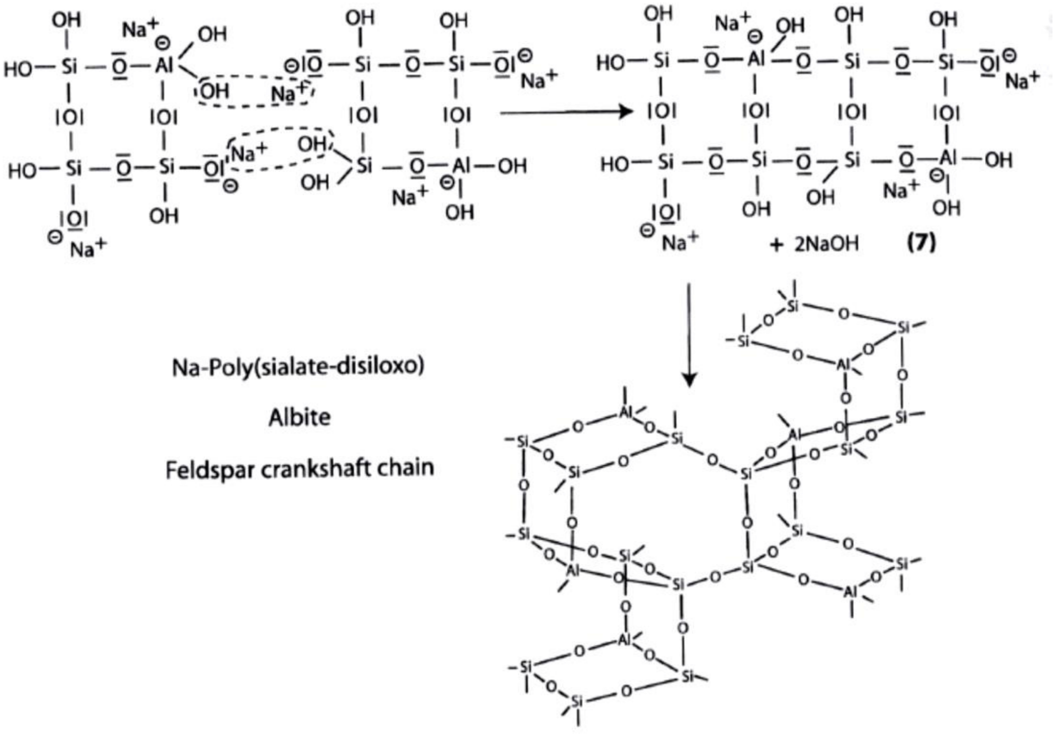
Step 7: *Polycondensation of branched quadratic di-(sialate-siloxo) molecules into Na-poly(sialate-siloxo), Na-PSS, phillipsite framework.*

<u>*For Si:Al = 3 the geopolymer framework is Na-poly(sialate-disiloxo)*</u>

Step 6: *condensation between di-siloxonate Q1 an ortho-sialate molecules, reactive groups Si-ONa, Si-OH and aluminum hydroxyl OH-Al-, creation of ortho-sialate-disiloxo cyclic structure, whereby the alkali NaOH is liberated and reacts again.*



Step 7: *further polycondensation into Na-poly(sialate-disiloxo) albite framework with its typical feldspar crankshaft chain structure."*



3.2 COLD SINTERING

In order to adapt a geopolymer based on the metakaolin-sodium silicate solution, to behave in a similar way to the kaolin-NaOH based system, the cold sintering approach and technology has been considered.

The sintering is the process which occurs during the thermal treatment and firing of traditional and advanced ceramics material. The primary thermodynamic driving force for sintering it the reduction in surface free energy, and sintering mechanisms are classified as either solid state or liquid phase, which involve diffusional process to bond the particles. To increase the driving force, pressure up to 200MPa could be used (e.g. hot pressing, hot isostatic pressing and field assisted sintering) or by enhancing diffusional process (e.g. flash sintering, microwave sintering).

The Cold sintering process (CSP) is a pressure assisted process, which permits to have dense ceramics materials (>90% relative density) at lower temperature than previously (<200°C) [46][47][48].

For this technology the sintering is possible using a solvent which possess a boiling point much lower than the ceramics sintering temperature. Acidic or basic aqueous solutions are the most used solvent. The solvent helps to decrease the energy required for the mass transport by a multistep mechanism, **fig. 3.1b**, thanks to a dissolution-precipitation process which could be considered a liquid phase sintering. The cold sintering is a hydrothermal assisted process. The CSP has been applied to hygroscopic substances, such as NaCl, NaF, CsBr, $NaNO_2$, KH_2PO_4, $BaTiO_3$ and alkali molybdates and phosphates, in which their structures easily react with the aqueous solution. The CSP can be described both at a macroscopic and microscopic level. The liquid phase is intentionally introduced at the particle-particles contact, after a mixing of the particles with an appropriate amount of solvent. The liquid phase behaves as a lubricant so by an external pressure, the solvent permits the particles rearrangement in a way that the sharp edges of the particles are partially dissolved into the liquid phase. At the same time the applied pressure gives the redistributions of the liquid phase into particles interstitials and pores, permitting an initial particles compaction in the first stage of sintering. Due to the solvent evaporation, the liquid phase is saturated, and the precipitation happens. The mass transport is enhanced by the pressure, ionic species and/or atomic clusters diffuse through the liquid and precipitate on particles. The mass transport permits to reduce the excess surface free energy and to remove the porosity forming a dense solid. Also, in some grain boundary area an amorphous could precipitate, limiting the grain growth of crystals. After the solvent evaporation, depending on composition and conditions, the amorphous phase may or may not crystallize. The described phases are shown in **fig. 3.1a**.

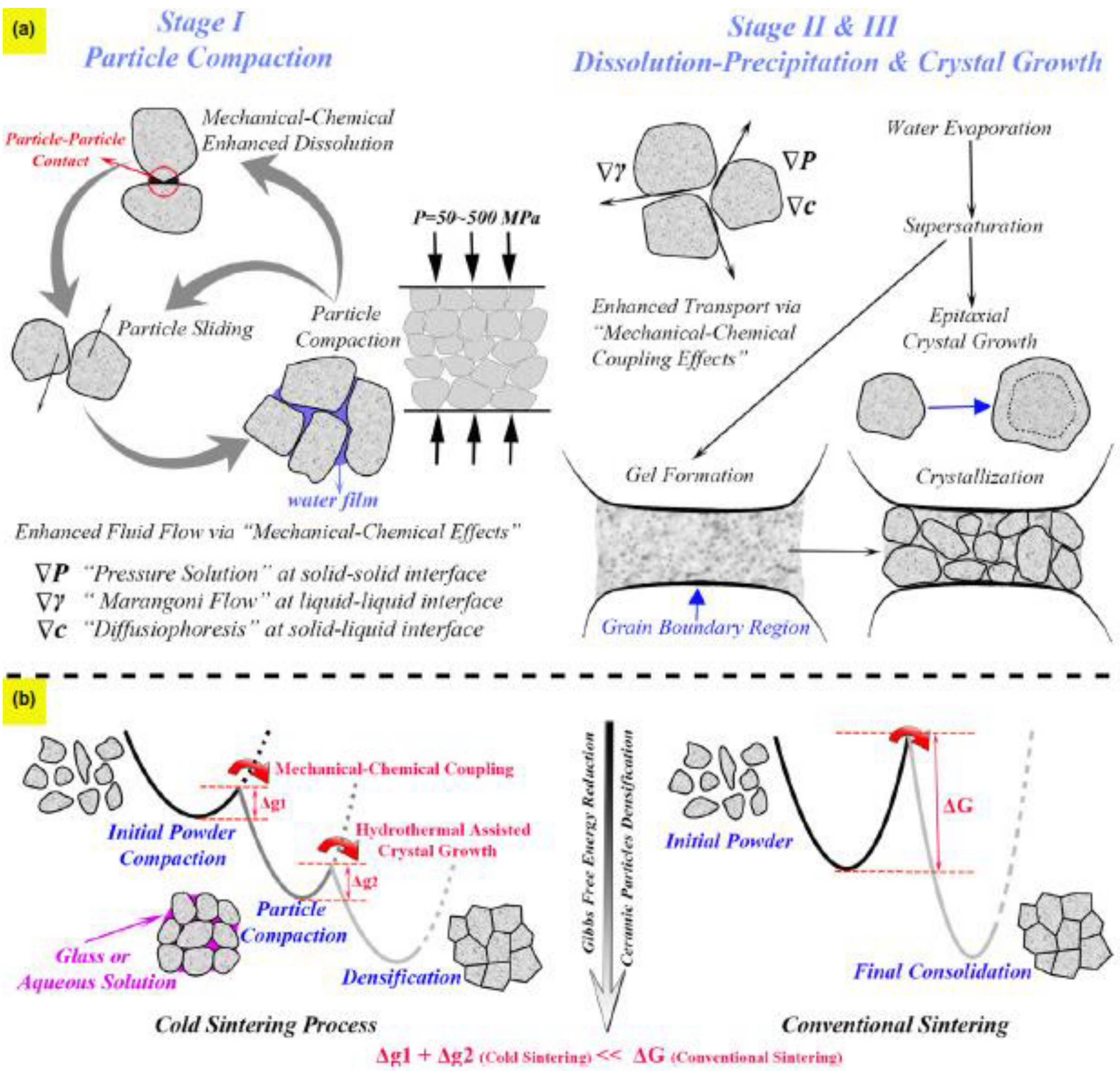


Figure 3.1: Macroscopic cold sintering phases (a); Gibbs free energy reduction comparison for CSP and conventional sintering [47]

Three type of mass transport in terms of diffusional process happen at microscopical level, as a function of the energy and surfaces involved in the process: liquid enhancedcreep at the solid/solid interface, Marangoni flow at liquid/liquid interface and diffusiophoresis at the solid–liquid interface. [47] On the hypothesis to work at a constant temperature, we don't consider the effect of temperature on the three proposed microscopic process.

The liquid-enhanced creep generally involves dissolution at intergranular interfaces and a diffusive mass transport, in which the dissolution occurs at the grain-grain contacts with the solute diffusing along the water film, and then it precipitates into the pore space as the liquid phase redistributes itself and fills into the grain–grain interstitials.

The Marangoni flow describes a mass transport along the liquid–liquid interface due to a surface tension gradient between them; this surface tension gradient can derive from a gradient of chemical concentration or a gradient of temperature. In a fixed temperature environment, since the dissolving of materials takes place at the water film layer close to the solid surface, Marangoni flow could be generated by concentration gradient, where the solute concentration in the aqueous solution gradually dilutes as it moves away from the solid surface.

Diffusiophoresis describes the transport of colloidal particles driven by a chemical concentration gradient of solute, and it does so by producing a slip velocity at the solid–liquid interface to drive colloids migrating through fluids. Generally, there are two types of diffusiophoresis: electrophoresis, involving with electrolyte systems, and chemiphoresis, in nonelectrolyte systems. Specifically related to the topic in this study, it has been known to be involved in crystal dissolution, crystallization, or evaporation and could involve the motion of aerosol. Marangoni flow and diffusiophoresis are similar phenomena but they happen on different interfaces.

The cold sintering possesses a high efficiency, because the TGA analysis show a loss in weight up to 1000°C, lower than 1% wt for the sintered samples. Using organic solvent like: C_{1-12} alcohol, ketone, ester the CSP could also be applied to polymer, so permitting the production of ceramic-polymer composites.

The CSP has been investigated for various system [48]. Pressure in the order of 200-500MPa and temperature in the range 120-180°C are the most commonly used conditions. To achieve pressing time < 60min the powder has to be smaller than 50microns.

3.3 COLD SINTERING OF GEOPOLYMER POWDER

In §3.1 we cited the reaction mechanism for the ratio Si/Al = 2 and 3 for the sodium based geopolymer. It has been widely investigated the effect of the Si/Al ratio on the properties of geopolymer materials [49], but related to the cold sintering of geopolymer, no works were reported in literature. "Zivica et al (2011)" [50] described the high-pressure compaction of a geopolymer paste based on the metakaolin-sodium hydroxide at pressure of 300MPa at RT. But the most interesting work which showed something similar to cold sintering, was the approach of "Takeda et al, 2014" [51], where using a warm press, dense geopolymer were obtained working in cold sintering condition so with very high pressure in the order of 200MPa, considering various temperature in the range 70°C-140°C and different pressing time. However for this work it was not possible to evaluate the exact composition of the geopolymer based on fly ash. They explained the densification of the geopolymer as a secondary condensation of the Al-OH and Si-OH unreacted groups which were present in the geopolymer amorphous powder after the drying, **fig. 3.2.**

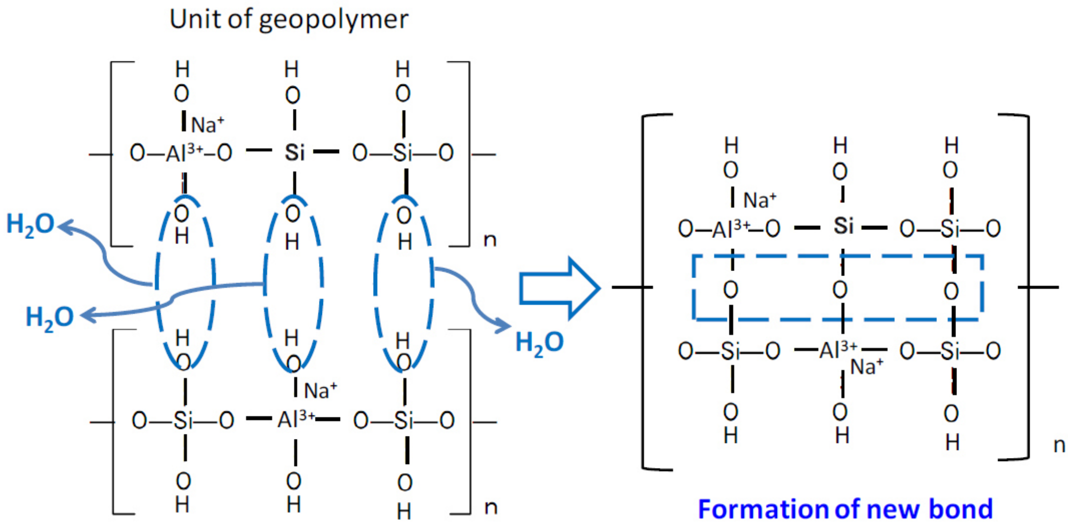


Figure 3.2: Conglomeration mechanism of geopolymer powder proposed by Takeda et al, 2014 [51]

So, with the idea to find an appropriate geopolymer composition based on the metakaolin-sodium silicate system, a Design of experiment (DoE) has been done in order to understand the effect of composition on the cold sintering of a geopolymer powder. However, we put a strong limit on the DOE, which was the value of the pressure used for the compaction, because the cold typical pressure value was much higher than the pressure used in the brake pads production technology.

The Design of Experiments approach has been used because the cold sintering of geopolymer was not yet studied deeply.

3.3.1 Basic description of Design of experiments (DoE) theory

An experiment or a series of tests are performed in all fields to improve or to discover something about a process/system. In engineering, experimentation plays an important role to develop new products like for the thesis work. The objective may be to develop process or products affect minimally by external sources of variability. However, research has a cost in terms of time, instrumentation and materials so a DoE helps to optimize the research. Different approaches can be defined to develop a DoE. For the present work we used the guidelines as described by: "D. C. Montogomery, Design and analysis of Experiments"[52].

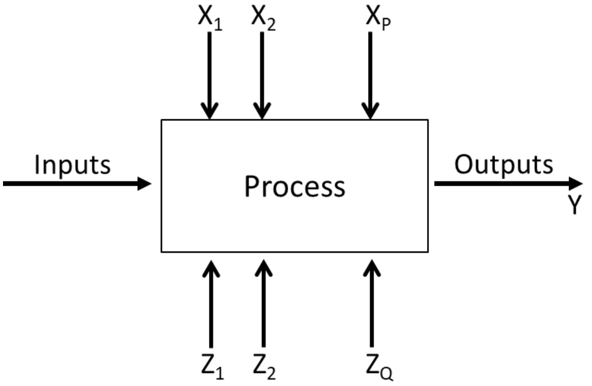


Figure 3.3: General model of a process or system

The **fig. 3.3** is a basic example of a process, which transforms some input (often a material) into an output that has one or more observable responses, Y. Some of the process variables are controllable, X, other are uncontrollable, Z.

DOE Step:

1) Recognition of the problem
2) Choice of factors, levels and range
3) Selection of the response variable

Steps 1), 2) and 3) are often done simultaneously. It is helpful to do a list of specific problems or question that are to be addressed by the experiment.

On the definition of factors X and level factor, it is important to distinguish the potential design factors from the nuisance factors. So, the potential design factor will be chosen for the experiment, and different factor level will be selected. Other factors could be considered held-constant factors, which influence the response, but they won't be considered during the experiment. It seems to be obvious but to choose the response variables, it has to be sure that these variables provide useful information about the process under study.

4) Choice of the experimental design

   Three basic principles have to be considered: replication, randomization and blocking.
   Replication: It is the repetition of a basic experiment and it is required to consider the variability of conditions and to estimate the experimental error. A confirmatory design will be used a replicated design, for investigatory analysis it is not required. Replication is not to repeat the measurement on a sample, but to re-produce the sample.
   Randomization: It requires that both the allocation of instrumentation/materials and the order in which the individuals run of the experiment are randomly determined. So, a pre-defined order for the run has not to be considered. Software help in this aspect, in particular by a random number generator which allow to create the list of the run.
   Blocking: It is a design technique used to improve the precision of the factor comparison. Often blocking is applied to reduce the variability due to nuisance factors. It permits to eliminate the factor which affect the experiment response but in which we are not directly interested, for ex. effect of raw material batches. Generally, a block is a set of relatively homogeneous experimental conditions.

5) Performing the experiment

   To minimize the errors related to the experimental procedure, it is suggested to conduct few trial runs, to check the measurement system, to practice the experimental techniques and to evaluate the consistency of the experimental materials.

6) Statistical analysis of the data

   Statistical methods should be used to analyze the data to have objective conclusions. There are many software packages designed to assist in the choice of the design (step 4) and in the statistical analysis, often by a graphical method.

7) Conclusion and recommendations

   After the experiment and the analysis of analysis, follow-up runs or confirmation testing should also be performed to valid the conclusions from the experiment. The experimentation should be iterative in order to have a major comprehension of the process studied by the DOE.

3.3.2 Design of experiment applied to geopolymer cold sintering

For this system and for all the studies we used as raw materials metakaolin and sodium silicate §1.1. To evaluate the geopolymer composition via in solution synthesis suitable to be used as matrix, a DOE in full factorial and un-replicated design was done. The DOE factors were related to the composition: SiO_2/Al_2O_3 ratio (5 value) and H_2O/Al_2O_3 ratio (3 value). It means to have 15 combination reported in **table 3.1.** A number was associated to each combination.

NC	SiO_2/Al_2O_3	H_2O/Al_2O_3
\	Molar ratio	Molar ratio
1	4.2	16
2	4.2	17
3	4.2	18
4	4.4	16
5	4.4	17
6	4.4	18
7	4.6	16
8	4.6	17
9	4.6	18
10	4.8	16
11	4.8	17
12	4.8	18
13	5	16
14	5	17
15	5	18

Table 3.1: Compositions investigated from the DoE

It is possible to observe how increasing the number associated to the composition, the SiO_2/Al_2O_3 ratio of the geopolymer composition increase.

We considered the compositions reported in table 3.1, because on the base of the reaction mechanism proposed by “Takeda et al, (2014)” and looking to the geopolymerization of Na-PSS and Na-PSDS, it appeared how increasing the Si/Al ratio, the Si-OH condensation become more important on the mechanism which control the geopolymerization. So, we considered increasing Si/Al ratio, because we supposed that the unreacted Si-OH groups should increase on the dried geopolymer powder, for higher Si/Al ratio. We did not consider higher Al/Si ratio to increase the Al-OH groups, because it was not possible to find a cheaper and reactive alumino-silicate as alternative to metakaolin. To increase the Al/Si ratio meant to use expensive pure Al source in form of reactive oxide or hydroxide. It was easier to increase the Si/Al ratio, changing the composition of sodium silicate solution.

At the same time, we considered different water content, in terms of H_2O/Al_2O_3 ratio, to evaluate if the unreacted Si-OH depends on the water content of the geopolymer material. To complete the discussion on composition, as described on geopolymer background, to have a stable geopolymer the Na/Al ratio was fixed equal to 1.

As requested from the DoE, we defined the following steps for the preparation of geopolymer samples considering the different composition:

1. Geopolymer synthesis: mixing of sodium silicate solution and metakaolin with a mechanical stirrer at 1000RPM for 10min
2. Curing at 40°C for 72h in close mold
3. Calcination at 150°C for 90min
4. Grounding of calcined geopolymer by ball milling at 450RPM to a dimension below than 200microns
5. Hot molding of powder at 150°C and 20MPa for 10min The same conditions of kaolin-NaOH studies
6. Analysis of data - ANOVA analysis

This method required a larger number of steps than the kaolin-NaOH system, but it solved the safety problems related to the free NaOH on the matrix and so on the friction formulation during the production of brake pads. At the same time this type of geopolymer powder was less hygroscopic than the kaolin-NaOH powder, solving the problem of the defects created on the brake pads during the production, for humidity content higher than 1%wt. Therefore, this approach was more industrially viable than the previous one based on the kaolin-NaOH system. The 3 value of H_2O/Al_2O_3 ratio were considered to increase the residual Si-OH groups and to tune the desired workability of the geopolymer paste, to don't give problem in terms of geopolymer paste homogeneity. In fact, increasing the Si/Al ratio a geopolymer paste becomes more viscous. In **fig. 3.4** is shown the mixing machine to produce the geopolymer paste.

Figure 3.4: Mechanical laboratory stirrer used to produce geopolymer paste

The geopolymer was stabilized with a calcination at 150°C to eliminate the excess of water. In **fig. 3.5** the calcined geopolymer blocks for the 15 compositions are reported.

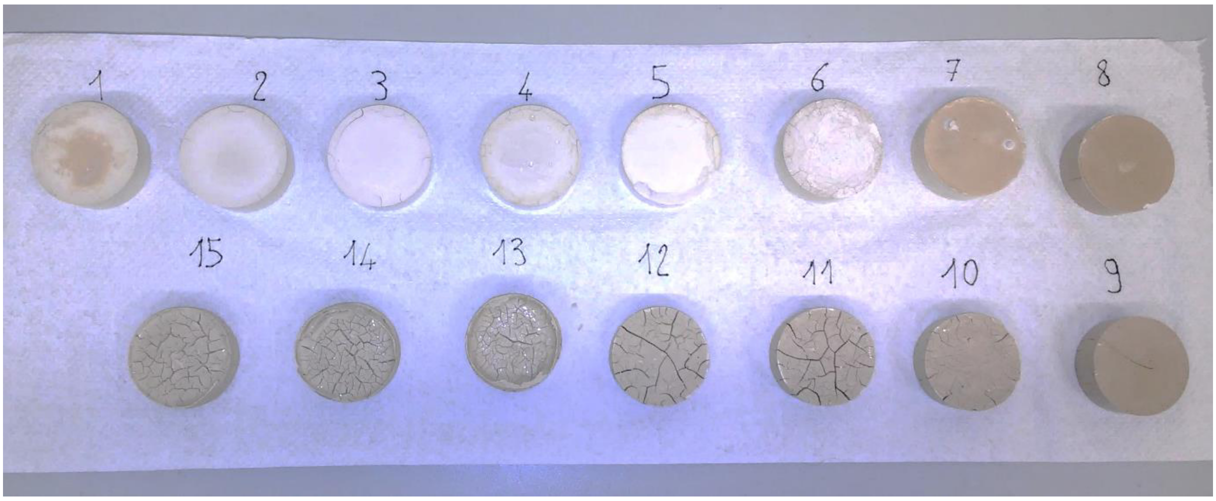


Figure 3.5: Geopolymer cured blocks after the calcination treatment, ordered in function of NC

For each composition at least 100g of ground powder below 200micron were produced, and 4 samples of 15g for each composition were pressed at 150°C 20MPa for 10min, with the same Struers Prontopress-2 warm machine used for the other system. In **fig. 3.6** a comparison of pressed samples for the different composition is reported.

Figure 3.6: Comparison of hot pressed geopolymer powder, ordered in function of NC

An interesting qualitative observation can be observed for the samples with the N° composition in the range 10-15. A major cracks content was observed for these samples after the calcination. And for the hot-pressed powder a changing in color and a major densification were observed. So, 15 un-replicated experiments were done. The response variables of the DoE were:

1. Hygroscopicity of ground powder.
2. Compressive strength
3. Density and porosity

Compressive strength, density, and porosity methods were described in §2.3. The hygroscopicity of the powder was measured as weight percentage of absorbed water in powder exposed to the air for 1h.

It is important to remember that the design was based on an explorative study, so we considered a full factorial and un-replicated design, considering more than 2 level for each factor. It permitted to have an exploratory analysis and to compensate the un-replicated design with the evaluation of more factor levels. This approach was used to evaluate if an important effect of the DoE factor was present in the system. The un-replicated design was related to the geopolymer synthesis, not to the characterization of specimens.

The data analysis was done by the software "Statgraphics XVII" and using the analysis of variance (ANOVA) to evaluate if there was a correlation and a statistical effect of the factor on the response variables. For the analysis the randomization of the data has been done and the ANOVA based on the main factor model was considered. To have a statistically significant effect the p-value of the ANOVA had to be lower than 0.05: p-value<0.05. In **tab. 3.2** are reported the p-value and R^2 of the DoE model in relation with the response variables.

Model	***Hygroscopicity of powder***	***Compressive strength***	***Porosity***
P-value	0,0000	0,0001	0,0000
R^2	97,35	95,02	97,64

Table 3.2: p-value and R^2 of the DoE model

The p-value for each response variable was lower than 0,05 so the model was statistically significant. It means that the main factor model is appropriate for this study. To have a confirm, repeating the analysis with a two factors interaction model, the p-value become major than 0,05. The R^2 suggested a strong correlation between the factor and the response variables. In **tab 3.3** is shown the p-value of the single factor considering the main effect model respect to each response variable.

DoE factor	***Hygroscopicity of powder***	***Compressive strength***	***Porosity***
SiO_2/Al_2O_3 – p-value	0,0000	0,0000	0,0000
H_2O/Al_2O_3 – p-value	0,4750	0,4964	0,8284

Table 3.3: p-value of the DoE factor

Considering the single factor effect we can observe how:

- The H_2O/Al_2O_3 ratio has not a statistical effect on the response variable
- The SiO_2/Al_2O_3 has an effect on all the response variable. The very low p-value < 0,0000 suggest how the effect of the SiO_2/Al_2O_3 of the geopolymer has a strong effect on the properties of the cold sintered geopolymer powder. In particular the for samples in the range 10-15, with a value of SiO_2/Al_2O_3=4.8 – 5.
- No optimization and extrapolation of the data have been done, because it was a preliminary/investigatory study

To put in evidence the effect of SiO_2/Al_2O_3 factor, all the response variables have been plotted in function of SiO_2/Al_2O_3 ratio. For an easier comparison we preferred to plot the response variable in function of the composition number (NC) of the table 3.1. In the graph in **fig. 3.7** porosity, apparent and geometrical density are plotted in function of NC. In **fig. 3.8** the effect on NC on compressive strength is shown, and the same in **fig. 3.9** where the effect on the powder hygroscopicity is reported as absorbed water percentage.

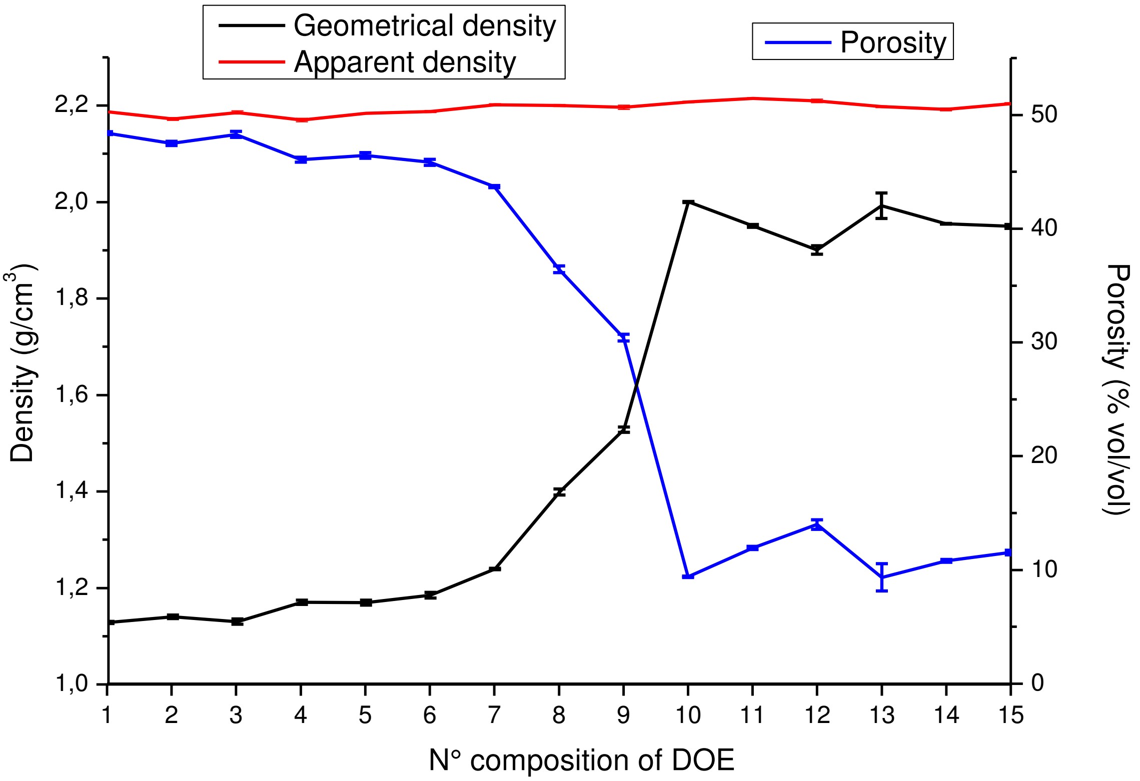


Figure 3.7: effect of NC on porosity and density of pressed geopolymer powder

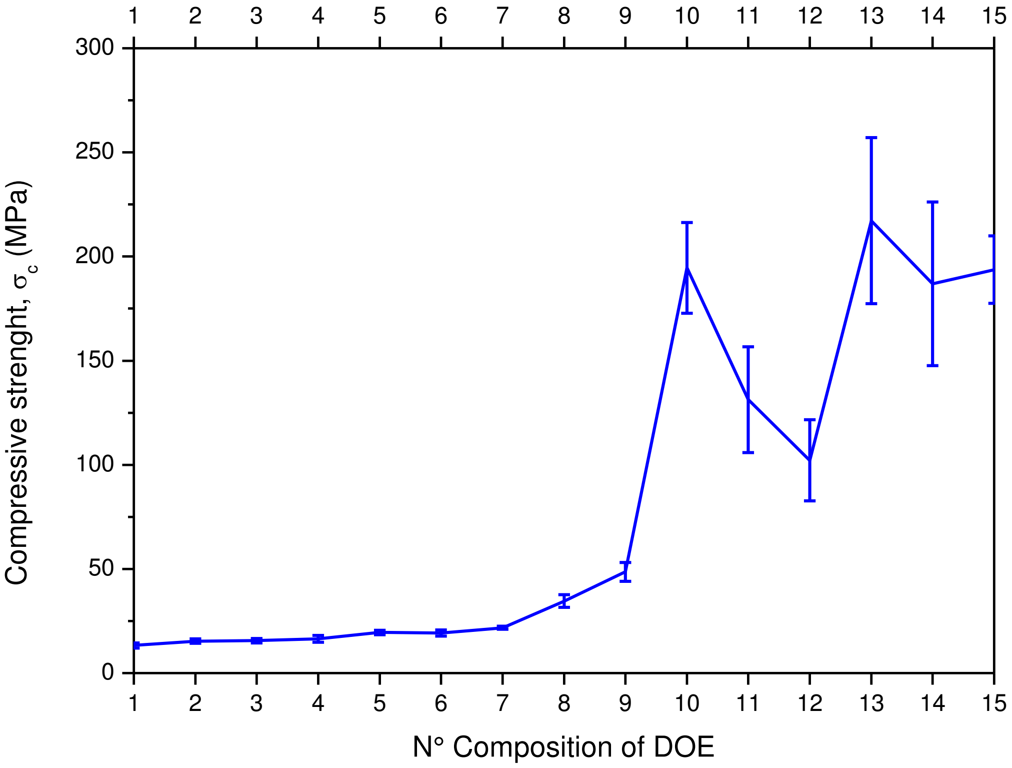


Figure 3.8: Effect of NC on the compressive strength of the hot pressed geopolymer powder

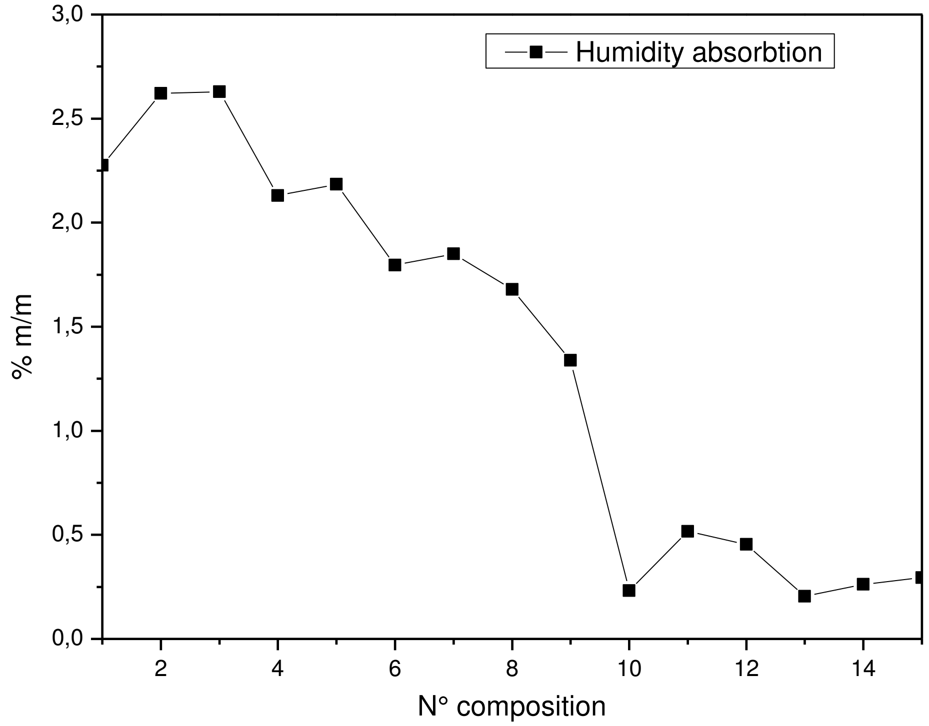


Figure 3.9: Effect of NC on powder hygroscopicity

From the graphs a strong effect of the SiO_2/Al_2O_3 ratio was observed. It appears how increasing the SiO_2/Al_2O_3 ratio, the densification was enhanced for the powder during the hot molding process. The porosity in fact decreased from a value of ≈45% vol/vol to 10% vol/vol for the samples with the highest Si content. The increasing in densification caused an improvement of compressive strength reaching the very interesting value of 200MPa, higher than the samples produced by "Takeda et al, 2014" but they used fly-ash and worked with pressures which were more than 10times the DoE pressure. At the same time, starting from powder smaller than 200microns a relative density of 90% was obtained, much higher than the normal geopolymer components, and requiring lower pressure and bigger particles than normal CSP.

An opposite trend was observed for the powder's hygroscopicity. The BET analysis was not done on the ground powder, so the surface area effect cannot be discussed. However it is interesting to observe how this type of geopolymer powder is much less hygroscopic than the kaolin-NaOH powder. For the 3kaolin:8NaOH after 1h the humidity absorption was the 10%wt. In conclusion the DOE permits to define the N°15th composition as the best in terms of mechanical properties and porosity, and with a hygroscopicity lower than the kaolin-NaOH system. The success of the DoE method was confirmed by the fact, that a geopolymer composition was found as a promising alternative to the kaolin-NaOH system, for the production of brake pads.

3.3.2.1 Chemical analysis on DOE NC15 sample

On sample NC15 chemical analysis has been done to evaluate the degree of the geopolymerization and the chemical stability and properties of the composition selected to produce brake pads.

In **fig. 3.10** is shown the XRD analysis on samples NC 3,6,9,12 and 15 of the DOE. Considering the absence of effect of the water content, the comparison has been done on the base of the SiO_2/Al_2O_3 ratio and for compositions with the same water content.

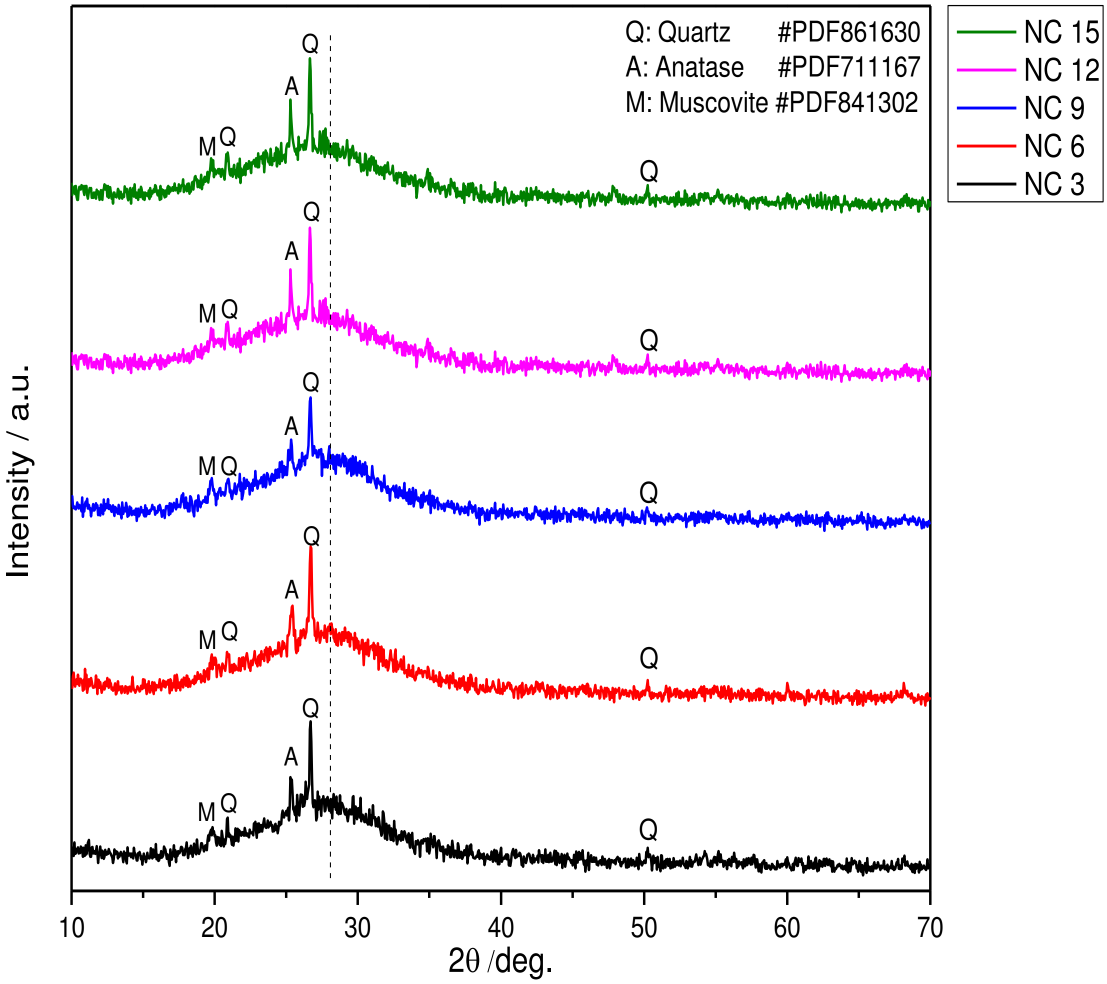


Figure 3.10: XRD analysis on sample 3,6,9,12, and 15 of the DoE

The geopolymer XRD analysis reported a mainly amorphous matrix with quartz, anatase and muscovite impurities typical of metakaolin based geopolymers not treated at high temperature [53].

Increasing the SiO_2 content, the amorphous region was shifted to lower angle, in relation with the more silicatic nature of geopolymer. It is confirmed by the XRD of NC 15, where the maximum of the amorphous region on the XRD pattern is located on the same position of the quartz main peak. To evaluate the stability of the geopolymer powder NC15 , FTIR and NMR analysis are reported in **fig. 3.11,fig. 3.12 and fig. 3.13.**

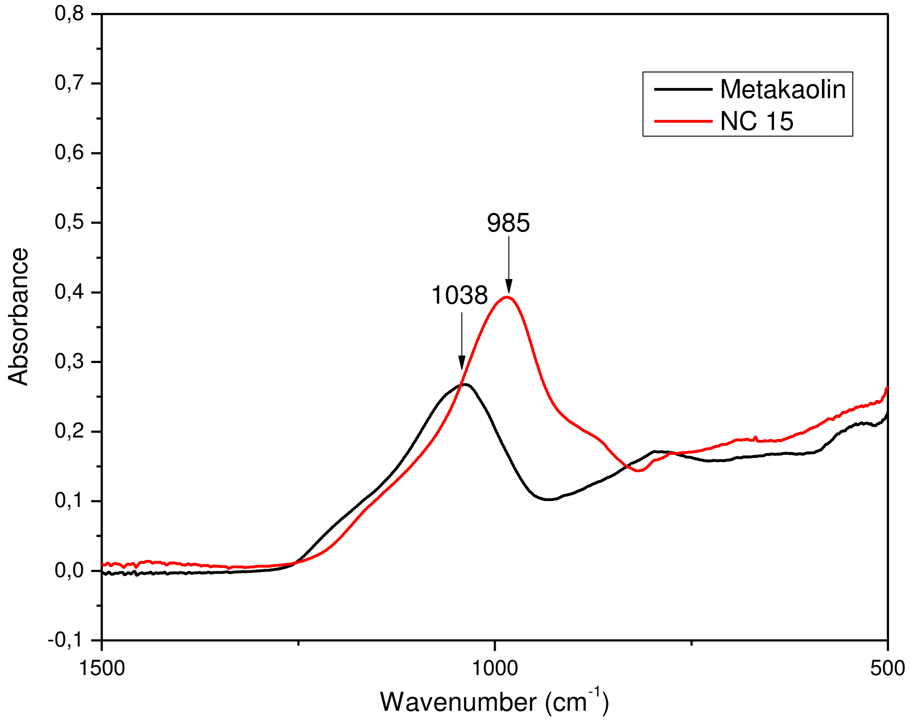


Figure 3.11: FTIR analysis on metakaolin and DoE NC15

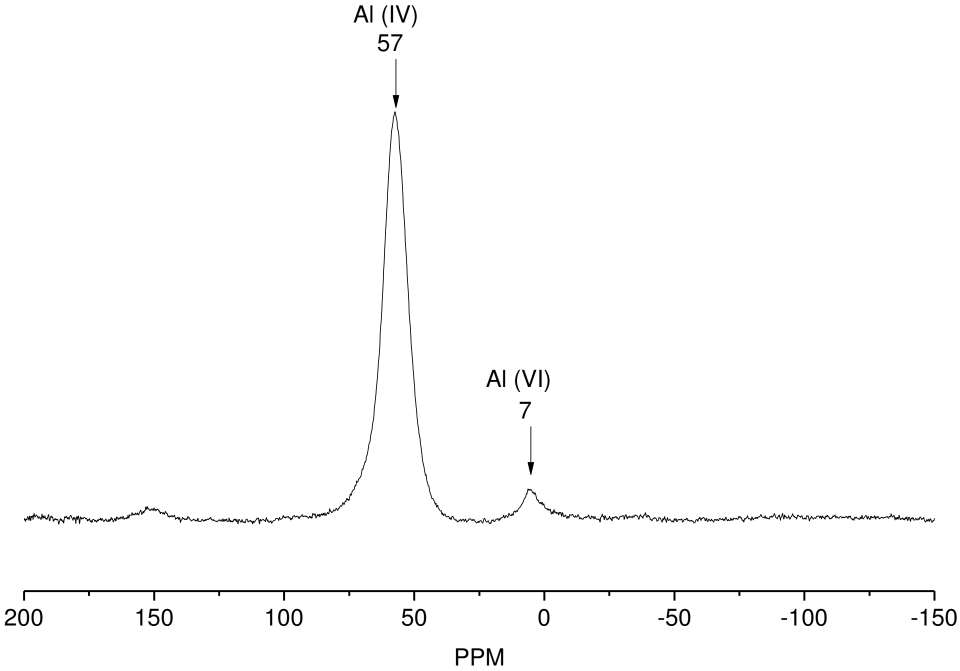


Figure 3.12: ^{27}Al MAS - NMR analysis on DoE NC15

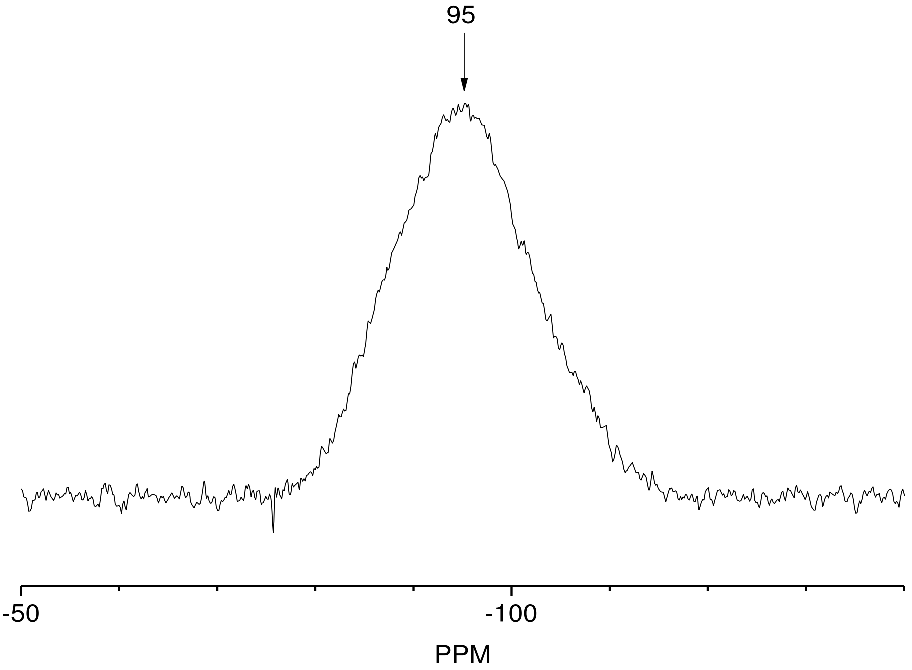


Figure 3.13: ^{29}Si MAS-NMR analysis on DoE NC15

The FTIR and NMR analysis showed how the geopolymer had a stable geopolymer network. For the FTIR analysis of geopolymer and aluminosilicate precursor, a peak associate to the vibration mode of the Si-O-Al or Si-O-Si is found at 950-1250cm^{-1}. This kind of vibration mode is sensitive to the Si:Al composition of the framework and the peak shift to a lower frequency with increasing number of tetrahedral aluminum atoms [27]. Comparing the spectra of the geopolymer NC15 with the metakaolin spectra, a shift of 53cm^{-1} was observed, confirming the geopolymerization and the dissolution of the metakaolin on the sodium silicate solution.

The ^{27}Al MAS- NMR analysis give a quantitative estimation of the Al coordination. For the NC15 geopolymer powder a very low residual amount of octahedral aluminum Al(VI) was found, compared to the four-coordinated aluminum Al(IV) which is related to the aluminum tetrahedra in the geopolymer structure. So the geopolymer network and the powder were stable, explaining the low hygroscopicity of this system.

As last measure the ^{29}Si MAS-NMR was done. A large broad peak was observed, and it was related the different coordination of Si with Al which could be find in the geopolymer network. Position and shape of the peak were comparable with previous studies [54][55], where NMR spectra were studied in function of the geopolymer compositions. Other peaks were not found, so no contributes from un-reacted metakaolin and sodium silicate were detected.

3.4 DEVELOPMENT OF BRAKE PADS

On the base of the interesting properties of the composition NC 15 of DOE a preliminary test to produce brake pads was done. For the brake pads production with the new system, as starting point we used the same optimized friction formulation developed for the kaolin-NaOH system. The test was done reproducing the DOE conditions so pressing at 20MPa and 150°C for 10min and using a degassing step as in the case of kaolin-NaOH system. It was done to eliminate the water produced by the cold sintering of geopolymer particles

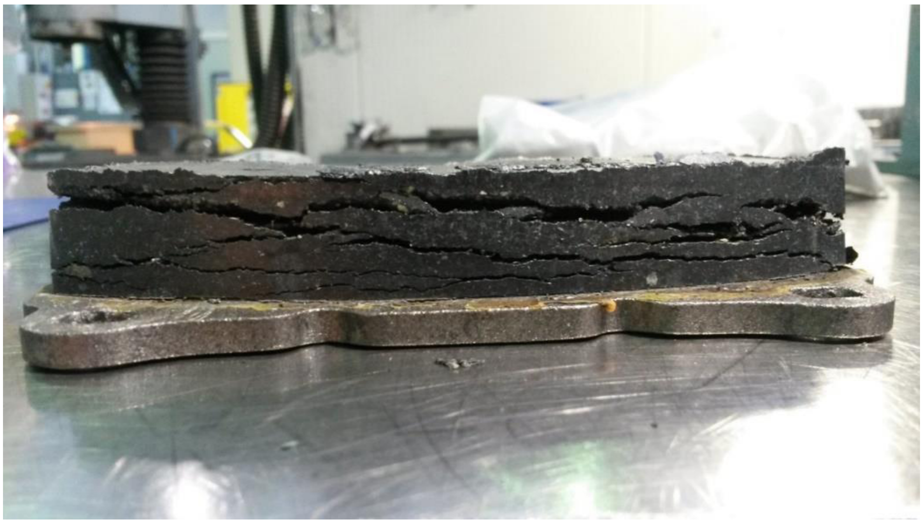


Figure 3.14: Preliminary test of a brake pad based on the cold sintering system

In **fig. 3.14** is shown a pressed brake pad. The material reacted, but also big cracks were present on the brake pads. The results of the test showed that:

- It was not possible to obtain brake pads with a good resistance and without cracks.
- The cracks formation was related to the release of a high amount of steam, due to the residual humidity in the geopolymer's powder. The degassing step did not permit to eliminate the excess of water remained in the geopolymer after the calcination.
- In the DoE study, the production of pure geopolymer component did not evidence problems of densification, so the presence of fibers and fillers in the friction formulation required a matrix with an optimal water content to enhance the densification behavior in order to have the formation of free cracks brake pads.

3.4.1 Optimization of powder's humidity for cold sintering

As shown for the kaolin-NaOH system the limit amount of humidity was 1%wt. It has sense to consider for the cold sintering a major amount of humidity to activate the reaction, but during the densification a smaller amount of water was produced compared to the kaolin-NaOH reaction. Therefore, there was an optimal range of residual water content after calcination, which permitted the densification of brake pads without cracks. So an optimization of the calcination process was necessary to have an accurate control the residual water content. To control the water content a setup configuration was defined. The geopolymer paste needed to be formed in a shape which permits to have a loss in weight during the calcination, ideally independent on the amount of material. It could be possible working with a high ratio surface/thickness to enhance a homogeneous evaporation and to didn't have difference from bulk and surface. The production of geopolymer wires was selected to have an optimal calcination. Due to the shape of the wires, which did not permit an easy way to control the curing, we decided to conduct the curing and the calcination at the same time, by the calcination treatment at 150°C. Thanks to the high temperature, physical properties, FTIR and NMR analysis didn't evidence any difference compared to samples of NC15 obtained with the DoE procedure. The wires were produced by a mortar gun as shown in **fig. 3.15**. The wires were extruded on a Teflon sheet and put in the oven for the calcination. The Teflon were selected for the good thermal and chemical resistance, considering the alkalinity of the geopolymer paste.

Figure 3.15: Mortars gun (left) and the calcined geopolymer wires (right)

The calcined wires were ground by ball milling. Then the powder sieved below 200microns was pressed at 150°C and 20MPa for 10min. Different calcination time have been investigated, to have different loss in weight and so to evaluate the effect of the calcination time on the mechanical properties of the geopolymer. The Brazilian test was selected to evaluate the resistance, because it caused the failure by an indirect tensile stress, so it was the method suitable to observe the effect of the calcination time on the same material. In **fig. 3.16** is shown the effect of the calcination time on the resistance, and in **fig. 3.17** the failure fracture of the cold sintered geopolymers.

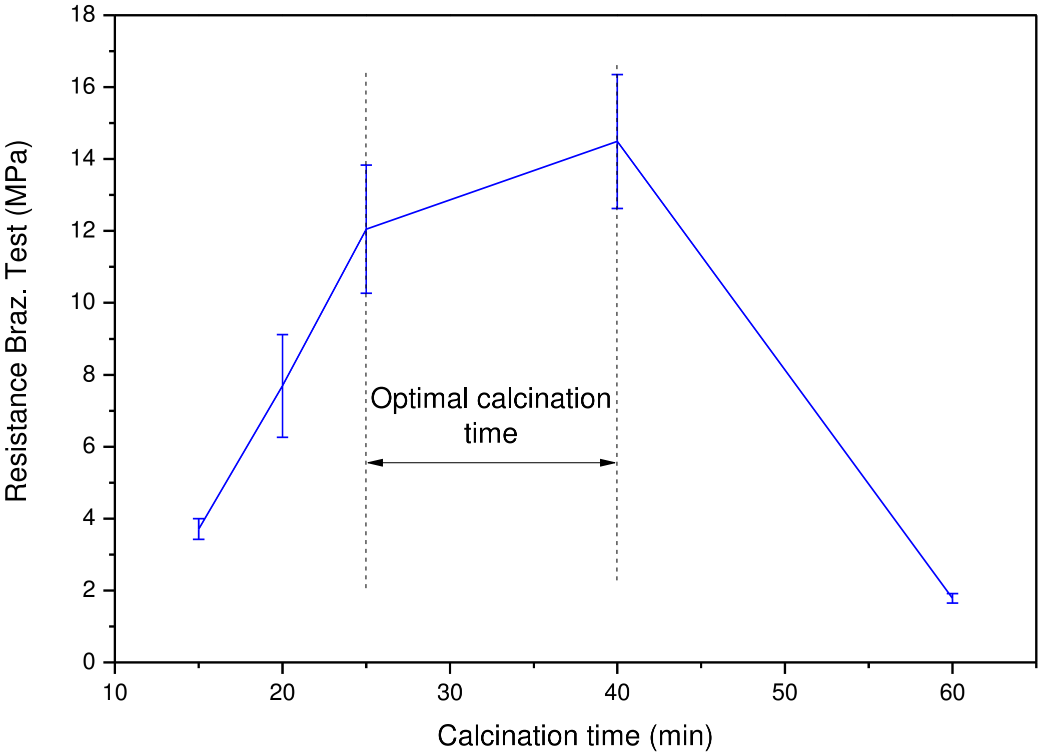


Figure 3.16: Effect of calcination time on the Brazilian resistance of cold sintered geopolymer

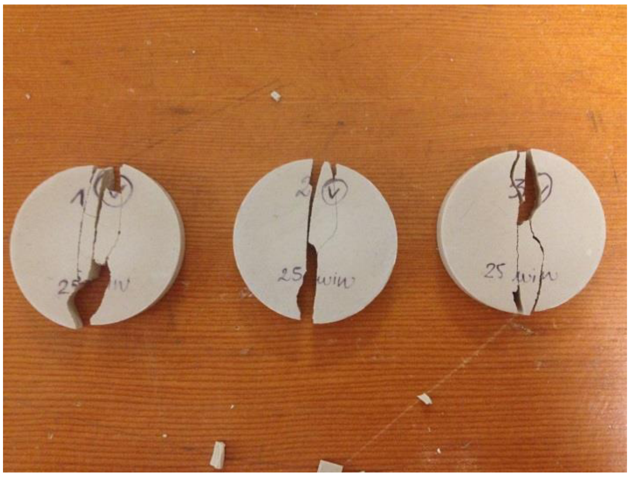


Figure 3.17: Failure behavior of cold sintered geopolymer obtained from a calcination time of 25min

An optimal calcination time of 25-40 min was defined to have the maximum value in terms of mechanical properties for the geopolymer components, in terms of Brazilian test resistance. It is also important to observe how for the powder treated for 60min too much water was removed, which didn't allow the activation of the cold sintering process. The failure observed for the specimens confirmed that the material failed for an indirect tensile stress, so the cold sintering gave the formation of an isotropic material. To complete the evaluation of the calcination time effect, the surface of pressed samples was observed by the stereomicroscope. In **fig. 3.18** are reported samples produced with powder having different calcination time.

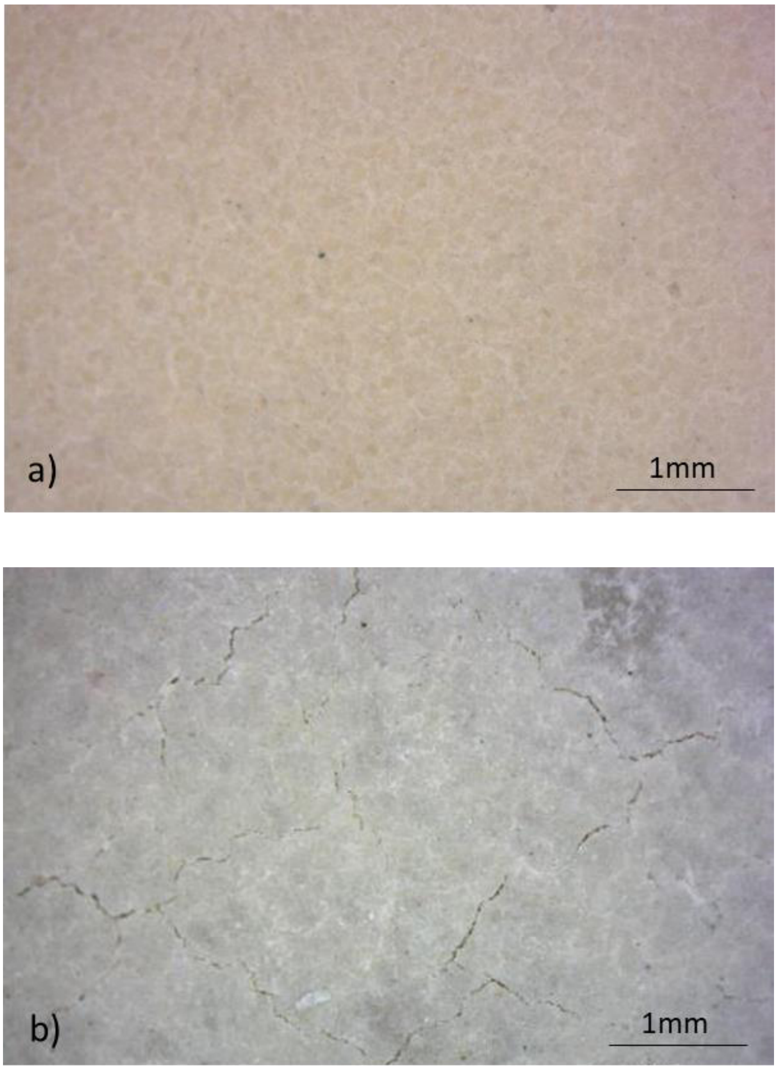


Figure 3.18: Hot pressed samples produced with powder calcined for 40min (a) and for 15 min (b)

The sample with the best mechanical properties had a surface without defect and cracks, and it is associated to 40min of oven drying. A calcination time of 15 min caused the presence of an excess of humidity. During the warm pressing and so during the cold sintering reaction the evaporation of the exceed humidity caused the formation of cracks, which were the reason for low resistance associate.

To evaluate porosity and quality of densification with higher magnification, SEM microscopy was used. However due to the effect of water content on the properties of the pressed materials, the vacuum pressure required for the system caused the evaporation of water from the bulk of the sample and the formation of cracks, as in **fig. 3.19**, so no considerations could be done.

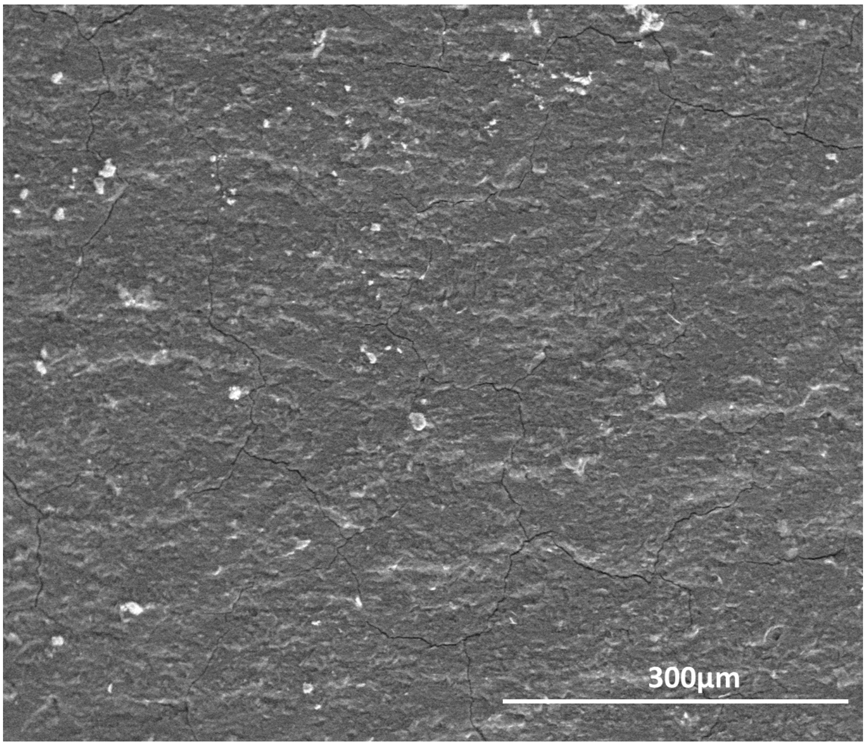


Figure 3.19: SEM image of a samples produced with a powder calcined for 40min

To evaluate the particles densification, the optical microscope with reflected light was considered. The technique required to prepare the surface of component to be planar and defect free in order to have a good reflection to evaluate in a properly way the surface. This microscope analysis was not commonly used for ceramic due to the difficult for brittle materials to prepare a planar and free defect surface by polishing. In **fig. 3.20** is possible to observe the polished surface of a cold sintered sample with the best properties. The image confirmed that the vacuum produced the cracks observed with SEM. At the same time on the image was not possible to distinguish the interface between the pressed geopolymer particles, so it was a confirm of the good densification occurred in the materials which remained amorphous after pressing, with no secondary crystallization, so the densification was related only to the Si-OH condensation.

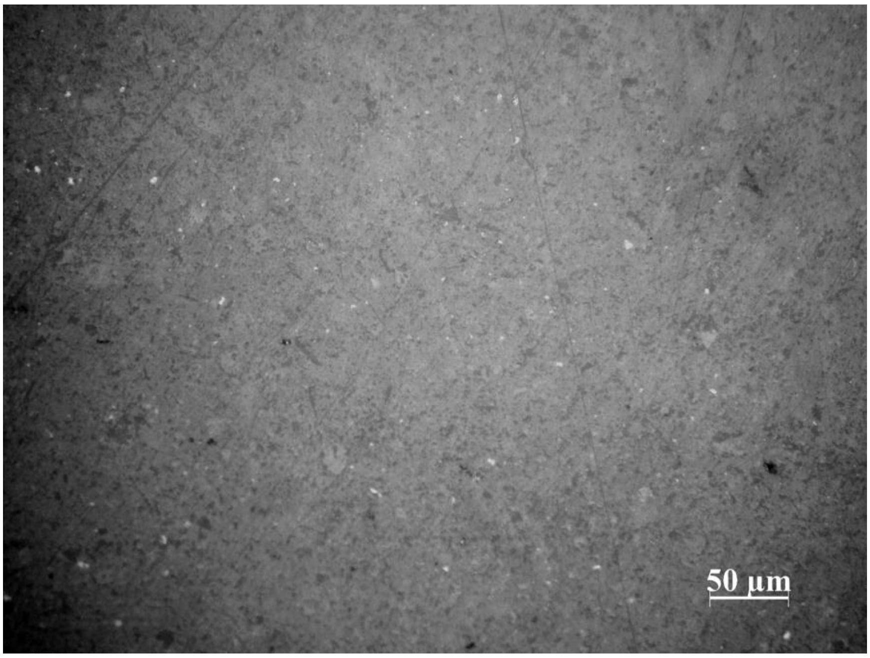


Figure 3.20: Optical microscope image of a sample produce with a powder calcined for 40min

3.4.2 Production of optimized geopolymers powder

Defined the best properties of the geopolymer powder in terms of composition and residual water content, the production of brake pads was investigated.

To produce a brake pads batch which permitted: to investigate the process condition, to evaluate different pressing time and to carry out the characterization of brake pads in terms of physical and friction properties, a geopolymer amount of 2kg was required.

However if no problems were related to the preparation of calcined geopolymer wires, the ball milling was not suitable to ground 2kg of materials, because long time should be required to grind and to sieve the powder. Thanks to the low hygroscopicity of this geopolymer composition, a jaw crusher was used to grind the calcined geopolymer wires, **fig. 3.21**. It grinds the materials by the movement of the jaw, permitting to work in continue and not with small batches of materials like for ball milling. The crusher is not a sealed system, so the operations were conducted in air, but it was not a problem for this geopolymer system. The minimum dimension limit of the jaw crusher is 100microns.

The crusher was considered because a granulometry comparable with the kaolin-NaOH was required. To produce particles lower than 300micron the crusher was appropriate.

During the last part of the project, for the cold sintering approach the goal was to evaluate if it was possible to produce brake pads based on this system. So, the crusher has been a preliminary approach to the scale-up of the geopolymer powder's production based on the cold sintering approach.

Figure 3.21: Jaw crusher Retsch BB50

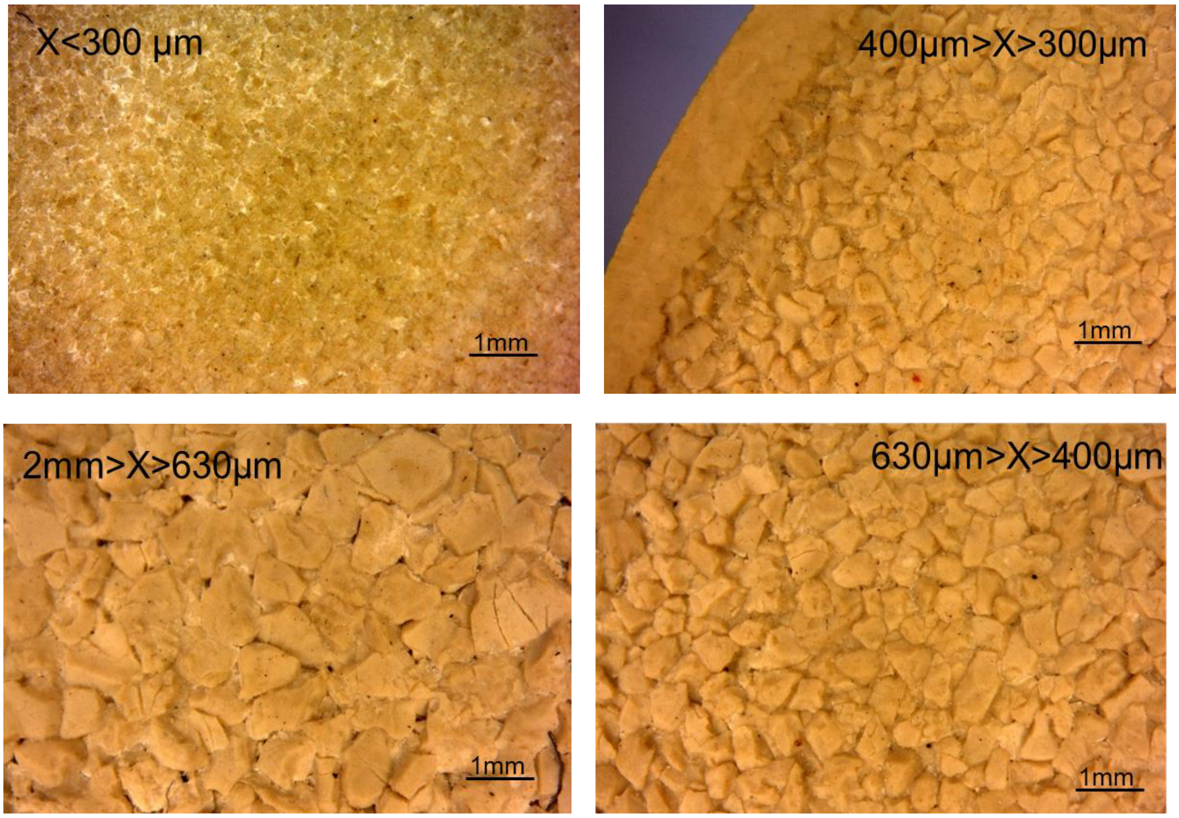


Figure 3.22: Surface images of cold sintered samples from powders with different granulometry

To produce 2kg of geopolymer ground powder, we started from 2,5kg of calcined geopolymer wired and with a calcination time of 40min. In this way we did not have to do many steps at the jaw crusher to produce the desired amount of powder below 300microns.
The remaining powder was sieved and divided in other 3 granulometry range:

- 400µm > x > 300 µm
- 630µm > x > 400 µm
- 2mm > x > 630 µm

The different granulometry range were pressed for 10min at 20MPa and 150°C used to evaluate the effect of the granulometry on the densification and on the resistance of the cold sintered powder. Five samples for each granulometry range were produced. In **fig. 3.22** are compared the surface of the pressed geopolymer components, and in **tab. 3.4** the effect of granulometry on porosity and mechanical properties were evaluated again by the Brazilian test.

Granulometry (microns)	**Apparent density (g/cm^3)**	**Porosity (%vol/vol)**	**Res. Brazilian test (MPa)**
X<300	2.13±0.01	4.98±0.02	15.70±1.89
400>X>300	2.13±0.01	9.19±0.01	10.85±1.38
630>X>400	2.13±0.01	9.37±0.18	10.74±2.67
2mm>X>630	2.12±0.01	8.46±0.03	10.78±1.44

Table 3.4: Effect of powder's granulometry on apparent density, porosity and resistance

As expected, working with a granulometry below than 300microns permitted to have the maximum value in term on resistance minimizing the porosity. For a granulometry bigger than 300micron the resistance decreased but it remained constant for the other dimension considered. Looking to the samples surface it appeared how the roughness increased with the granulometry, and bigger pores were located between the particles. The absence of a finer fraction did not permit to fill the space between the particles. So, it caused the formation of the pores with a decreasing in resistance. However, despite of the dimension of the pores in the order of 100-200 microns, the resistance remained at a good level, which was comparable with a powder smaller than 200microns but with a non-optimized water content, like the samples obtained from powder calcined for a time in the range of 20-25min. It confirmed that where the cold sintering happened, a strong bonding between the particle occurred. In fact, on the base of the Brazilian test resistance, a powder sieved under 300microns has an effect comparable with the powder sieved below 200microns.

3.4.3 Brake pads based on the optimized geopolymers powder

Using the NC15 powder with the optimal residual water content, it has been possible to produce brake pads with the same optimized formulation developed for the kaolin-NaOH system. The substitution of the geopolymer matrix permitted to observe the brake pads in **fig. 3.23** which were pressed at 20MPa and 150°C for 7min.

Figure 3.23: Brake pads based on the geopolymer powder with the optimal water content

Some free cracks sample were produced and with promising properties, but to have hardness and stiffness comparable to the aftermarket and kaolin-NaOH based brake pads, a pressure value of 70MPa was required in order to enhance the densification. It allowed to decrease the pressing time to 5min.

Having a limited amount of geopolymer, we could not develop a specific friction formulation for the new geopolymer composition, so we used the same mix optimized for the NaOH-kaolin system. The presence of fibers and fillers inhibited the densification, but as expected from a system based on the sintering phenomena, temperature and pressure could compensate for the limit related to the presence of formulation's ingredients. Compared to the geopolymer powder, the phenolic resins did not possess this limit, because during the hot pressing step, the temperature enhanced the viscous flow of the resin, and the pressure allowed to the liquid resin the infiltration of the friction formulation. Thanks to the optimized cold sintering behavior of NC15, an increasing of the pressure permitted to have brake pads that we could characterized in terms of friction properties.

However the available geopolymer powder amount was limited, so to have an appropriate comparison of the cold sintering system with the kaolin-NaOH based brake pads and the aftermarket commercial product, the project moved from brake pads of the front axle, to the brake pads of the rear axle of the vehicle considered for the studies. In fact, brake pads for rear application are in general smaller than the front, so it has been possible to produce more pads to conduct and complete the required friction and wear characterization. In **fig. 3.24** is reported the new pad geometry which required approximately the 60% of the friction material used for the front axle brake pads.

Figure 3.24: Rear axle brake pads based on the new geopolymer composition

No aging effect due to the humidity absorption was found with this system, because we worked with a reacted geopolymer powder so, the hygroscopicity observed for the kaolin-NaOH system material was not present in the new composition. The cold sintering-based formulation permitted to have the same storage system used for the phenolic based friction formulation. Also, the new geopolymer composition solved the safety issue related to the handling of NaOH powder.

3.4.4 AK-master and TL110 characterization results

The AK.master and TL110 friction test results, for the friction formulation based on the new system, are reported in **fig. 3.25** and **fig. 3.26** and compared with the kaolin-NaOH based brake pad and with an aftermarket product. The comparison could be done only for pads having the same geometry, so rear brake pads based on the basic sodalite matrix were produced, where the matrix composition was 3kaolin:8NaOH. The pads were pressed at 150°C and 20MPa for 7min. The aftermarket was a friction formulation specifically developed for the described rear axle brake pad geometry. The same comparison has been done for the Wolverine test.

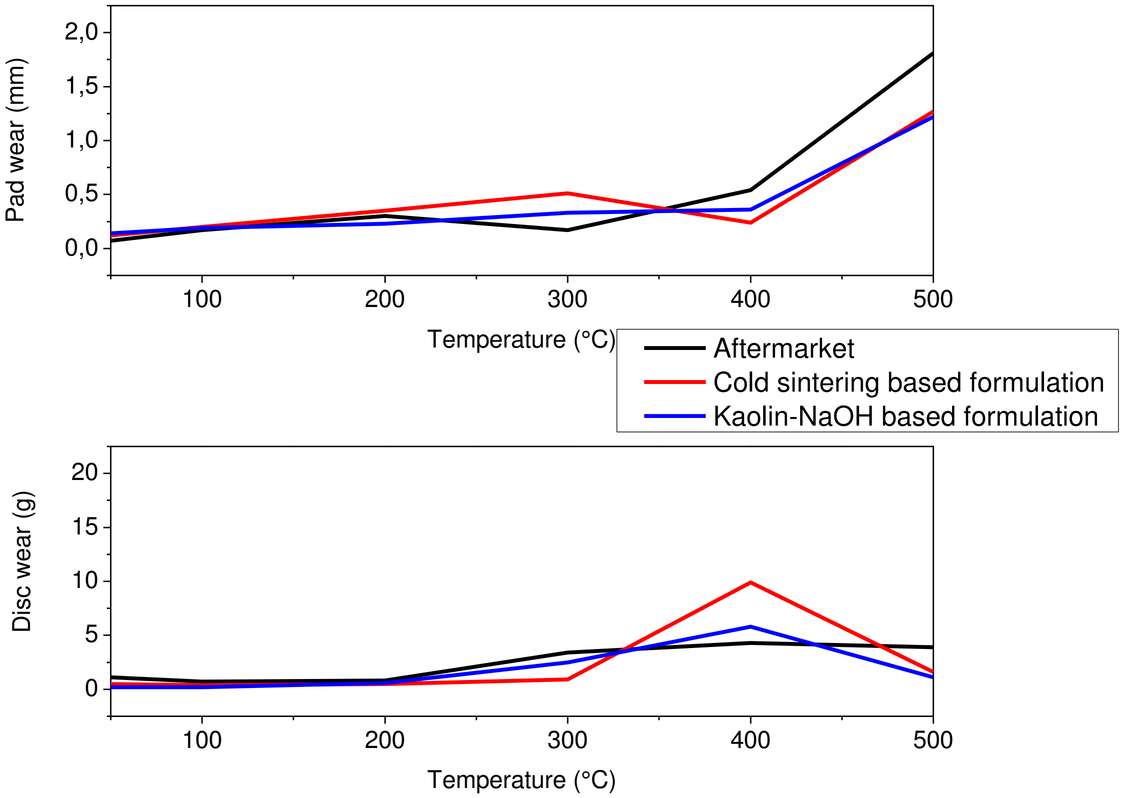


Figure 3.25: AKM - TL110 test: pad and disc wear compared for the different formulations

The AKM – TL110 results showed how the different friction formulation had not significant differences, despite of an increasing of the disc wear for the geopolymer-based friction formulations. From the AK-Master test appeared how the Aftermarket was developed in function of this pad geometry and application, because a low variability was observed. In particular the geopolymer formulation had a major sensitivity to the Recovery 1 (14) and the following step on the pressure sensitivity at 100°C.

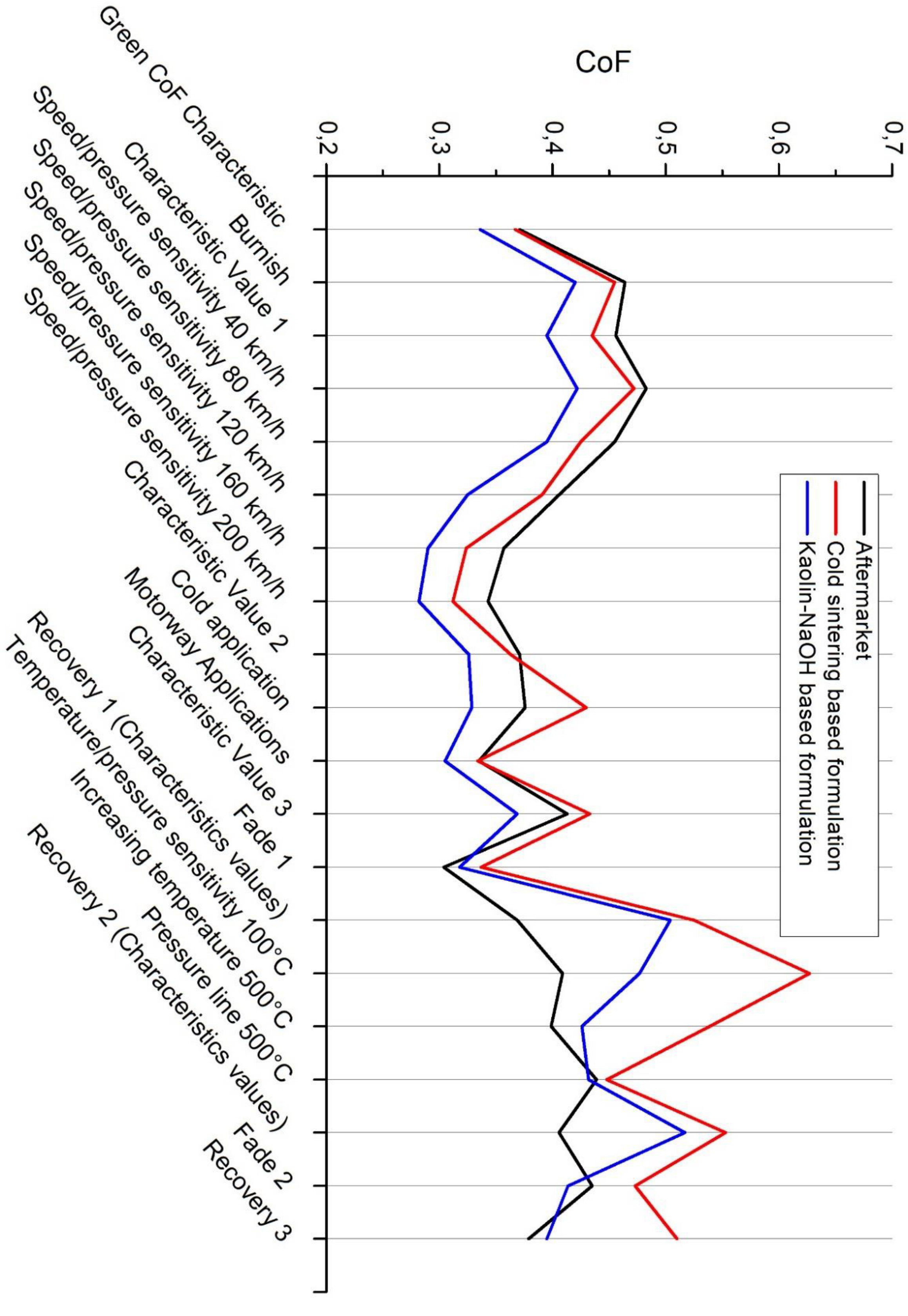


Figure 3.26: AKM test: Comparison of the behavior in terms of CoF for the different formulations

But it’s important to observe the best fade resistance of the cold sintering-based brake pads (Fade 1, Fade 2). In general for the other AK-Master phase, the behavior was similar for the different formulation, showing how the optimization have been done both on the geopolymer matrices and on the friction formulation, during the project.

3.4.5 Wolverine test results

In **fig. 3.27** and **fig. 3.28** are shown the graph of the Wolverine test and the pads at the end on the test.

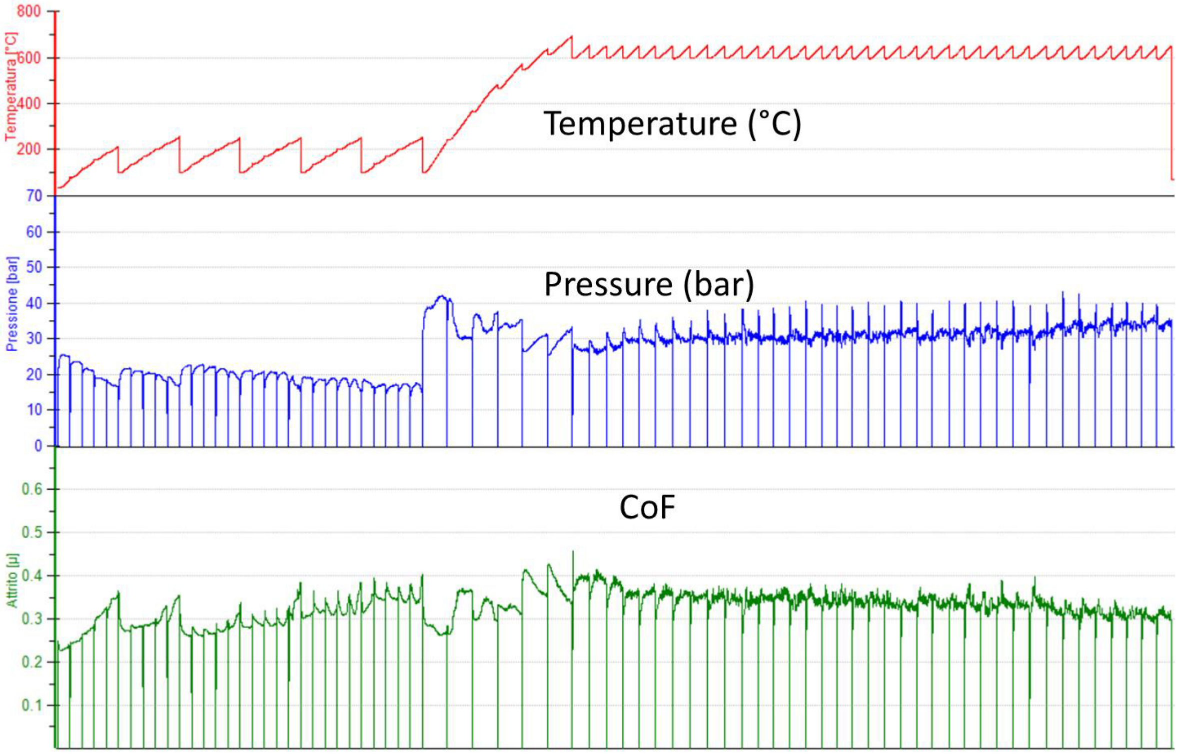


Figure 3.27: Wolverine test of the friction formulation based on the cold sintered geopolymer powder

Figure 3.28: Brake pad at the end on the Wolverine test: the pad passed the test

The results showed how the friction formulation based on the cold sintering of geopolymer powder had not problem and passed the Wolverine test, for pads pressed for 5min during the production. No cracks on the pads were observed at the end of the test, and the CoF is almost constant for all the test, showing a good stability of the material at 600°C.

This type of geopolymer composition did not have a residual amount of a reagent which could degrade at temperature close to 600°C as kaolin. Because the geopolymer powder has just reacted during the synthesis of the geopolymer material.

The Wolverine test permitted to put in evidence, the key point of the cold sintering approach. In fact it was not required a minimum pressing time in order to have the conversion of the geopolymer precursor powder like for kaolin-NaOH system.

So for the cold sintering based friction materials, a pressing time comparable with the phenolic-based brake pads, could be considered.

CONCLUSIONS

The previous chapters demonstrated the feasibility of using geopolymers as matrix for brake pads, in substitution of the organic resins used as matrix on the commercial brake pads.

Two interesting classes of geopolymer compositions have been studied and developed and brake pads based on these compositions were produced.

The project has been financed from a company, so the geopolymer compositions have been developed considering a requirement of the company, that no modifications on the production process of brake pads had to be done.

The first geopolymer system was based on the hydrothermal reaction in absence of water of kaolin with NaOH, to have the formation of basic sodalite. The geopolymer system requires a simple preparation method, based on the dry or wet mixing of kaolin with sodium hydroxide. The dry process was preferred and an industrial machine as the jar rotator technology was chosen to mix the kaolin and sodium hydroxide.

A friction formulation based on this geopolymer composition was developed, by mixing of kaolin and sodium hydroxide with the other ingredients of the formulation. In fact, the hydrothermal synthesis happened during the hot-pressing step for the production of brake pads. The formulation was developed, optimizing the physical properties and the friction behavior of the brake pads.

However, it was difficult to have a low residual kaolin content in the pads formulation, in order to have acceptable friction properties in terms of high energy friction test, as the Wolverine test, because at 550°C occurred the degradation of the un-reacted kaolin.

To reduce the residual kaolin content, high NaOH content and long pressing time were required, but from the industrial point of view it has no sense to work in these conditions. Due to the high hygroscopicity of the NaOH present in the system, the handling of the friction formulations was difficult, so a second geopolymer composition has been developed.

The second system was based on the production of a geopolymer obtained from the reaction of metakaolin with a sodium silicate solution. The geopolymer was then calcined and ground and the powder used as matrix for brake pads. The consolidation mechanism of the powder was based on the cold sintering process.

So, for this method more steps to prepare the geopolymer matrix were required, but tuning composition, the residual water content and the granulometry of the geopolymer powder, it has been possible to use the same friction formulation developed for the kaolin-NaOH system, substituting the type of geopolymer matrix.

However, working with the second geopolymer system as matrix, better friction properties at high energy were obtained, compared with the basic sodalite-based friction formulation.

At the same time, it solved the safety problem related to the handling of the sodium hydroxide powder used in the kaolin-NaOH system. Moreover, the lower alkalinity and hygroscopicity of the new system permits to have a friction formulation easy to storage and without the absorption of humidity.

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