

# Products of hydration in fine grained mixtures $\text{MgO}$ - $\text{SiO}_2$ .

**J Szczerba<sup>\*1</sup>, R Prorok<sup>\*2</sup>, D Madej\*, E Sniezek\***

\* AGH University of Science and Technology  
Faculty of Material Science and Ceramics  
Department of Ceramics  
al. A. Mickiewicza 30  
30-059 Krakow

**E-mail:** <sup>1</sup> jszczerb@agh.edu.pl; <sup>2</sup> rprorok@agh.edu.pl

**Abstract** The aim of this study was to evaluate the influence of time of ageing on phase evolution of paste from  $\text{MgO-SiO}_2\text{-H}_2\text{O}$  phase system. The paste was composed of fine grained sintered magnesia and microsilica in 1:2 molar ratio and water, with water to solid ratio equal 0.5. After preparation the paste was ageing during specified time up to 180 days in temperature 20° C. Phase composition of mixture of  $\text{MgO}$  and  $\text{SiO}_2$  with water was studied by XRD, DTA-TGA. The analysis revealed that product of reaction in mixture of  $\text{MgO}$ ,  $\text{SiO}_2$  and water was a probably poorly crystalline magnesium silicate.

## 1. Introduction

One of the most important products of refractory industry are materials based on  $\text{MgO}$ . This kinds of refractory materials are used mainly in metallurgy as well as in cement and lime industry. Nowadays these industries used mostly shaped magnesia bricks but there are efforts to develop new kinds of refractory materials based on  $\text{MgO}$ . This efforts are mainly focused on basic castables based on  $\text{MgO}$ .

Magnesium oxide used in refractory industry is mineralogically name periclase and commonly called magnesia. Thank it is features like high refractoriness, (approximately 2840°C), high resistant to basic slags and environment, it is one of most important raw materials used to production of refractories[1, 2, 3]. But the magnesium oxide by it is ability to hydration is not suitable to production of good quality castables. To solve this problem, there can be used many substance that control process of hydration, one of such substance is microsilica. This characteristic of microsilica caused great interest in  $\text{MgO-SiO}_2\text{-H}_2\text{O}$  phase system, as base for designing castables based on  $\text{MgO}$ .

In reaction microsilica, magnesium oxide and water forms the magnesium silicate hydrate gels (M-S-H). This reaction is connected with formation of silicic acid ( $\text{HSiO}_3^-$ ) which is adsorbed on the magnesia surface. On the surface of  $\text{MgO}$  grains, silicic acid can react with  $\text{Mg(OH)}_2$  and creates poorly crystalline phase, determined as magnesium silicate hydrate (MSH). Formed phase surrounds grains of magnesia and prevents from its hydration [4].

The aim of this study was to define product of hydration of pastes from  $\text{MgO-SiO}_2\text{-H}_2\text{O}$  phase system, ageing for different time.

## 2. Experimental

Sintered magnesia (Nedmag, Netherlands) and microsilica (Elkem 995 U, Norway), in 1:2 molar ratio, were used as the starting materials. The study include preparation of paste with water, with water to solid ratio equals 0.5. Median grain size distribution of the raw materials were, for magnesia 18.5  $\mu\text{m}$  and for microsilica 0.263  $\mu\text{m}$ .

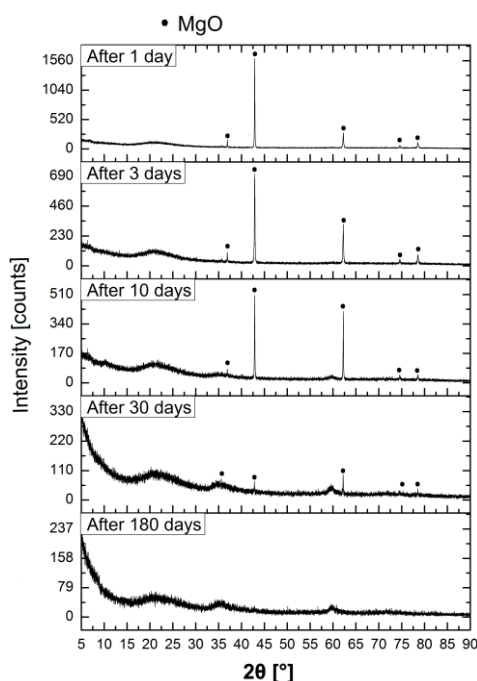
The obtained homogenous mixture of magnesia and microsilica powder was ageing up to 180 days. All the samples were ageing in sealed polyethylene bags at temperature 20°C. After an appropriate time, from paste was remove free water. After removing of free water, samples of the paste were subjected to examination. The examination of the ageing paste, included thermal analysis and XRD



analysis. Differential thermal analysis DTA, thermogravimetric analysis TGA and evolved gas analysis EGA, were performed in the range from 20°C up to 950°C with increasing temperature rate 10°C/min (Netzsch STA 449 with mass spectrometer Netzsch QMS 403). XRD analysis was carry out in range  $2\theta^\circ = 5-90^\circ$  (Panalytical X'Pert-Pro diffractometer).

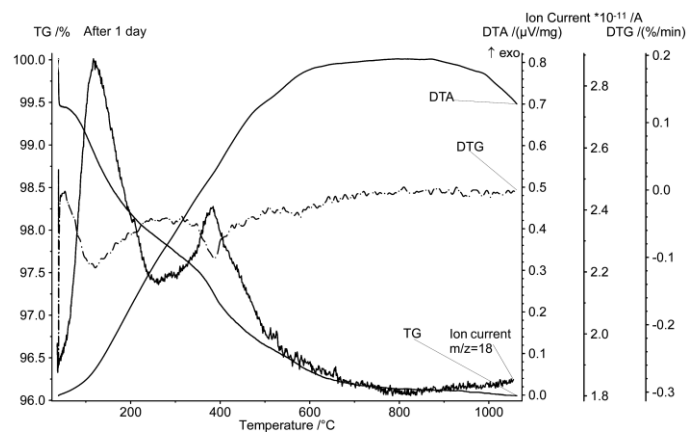
### 3. Results and discussion

XRD patterns for samples ageing up to 180 days at temperature 20°C are shown in figure 1. From XRD analysis there can be seen that the main phases, up to 3 days, are periclase (MgO), and after 10 days of ageing also the MSH phase (at  $2\theta = 23-30^\circ$ ,  $35-39^\circ$ ,  $58-62^\circ$ ). From XRD analysis can be notice that with time intensity of peaks from magnesia decrease while the intensity peaks from MSH phase increase. XRD analysis do not reveals present of expected brucite ( $\text{Mg}(\text{OH})_2$ ), which can indicate that the brucite is used in process of synthesis of MSH phase. The XRD analysis shows that probably in process of phase evolution in examined pastes, periclase is converted in to the brucite which at the same time is transform in to MSH phase, that why brucite is not detected on XRD analysis.

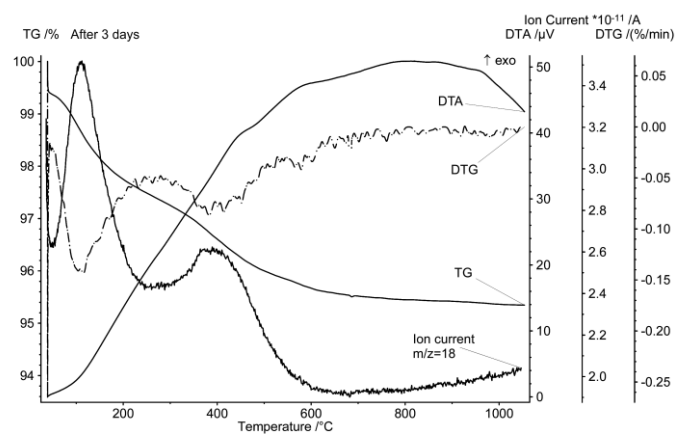


Figures 1. XRD spectra of samples ageing up to 180 days.

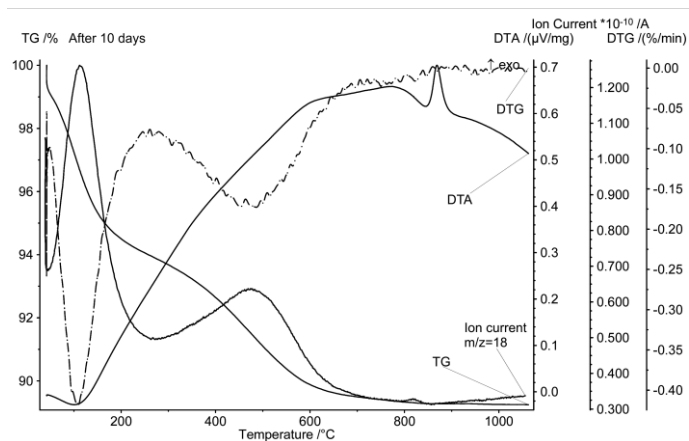
The thermal behavior of the examined samples is shown on figures 2-6. The DTA-TGA-EGA analysis for samples up to three days shows three main effects. First of them is endothermic effect, which occurs in the temperatures range up to 100°C. This effect is related to adsorbed water. Second effect at about 400°C, is probably related to decomposition of the brucite. However the effect from the brucite is almost not visible on the DTA curves but marked on TG and EGA curves, as mass loss connected with water secretion. This effect for sample ageing for longer time over 10 days is disappeared, but simultaneously in temperature range from 400°C up to 650°C, appeared another broad effect connected also with loss of mass and water secretion. There is no any significant changes on DTA curves in this area, but this effect may be related to decomposition of the seeds of hydrated phase. The last effect that occurs at about 850°C, is exothermic effect probably connected to synthesis of mixture of forsterite and enstatite. For samples ageing over 10 days (figures 5-6) the last effect is correlated with endothermic effect probably from dehydroxylation of low crystallite phase. The results of thermal analysis of studied paste are in agree with results of XRD examination.



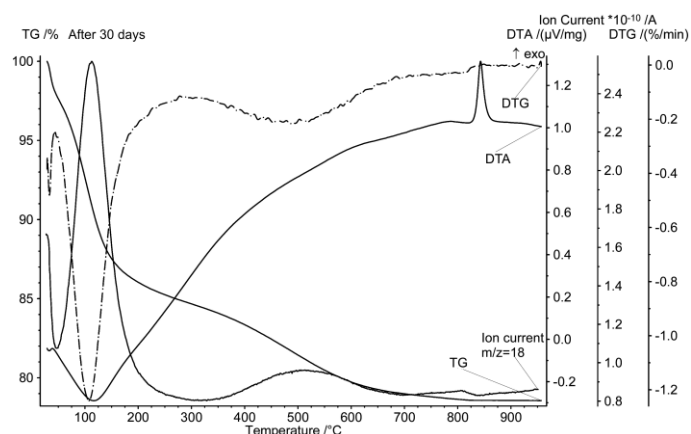
Figures 2. Thermal analysis of samples ageing for 1 day.



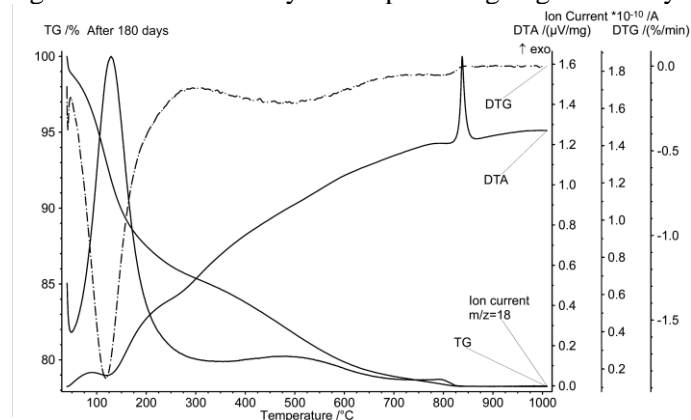
Figures 3. Thermal analysis of samples ageing for 3 days.



Figures 4. Thermal analysis of samples ageing for 10 days.



Figures 5. Thermal analysis samples of ageing for 30 days.



Figures 6. Thermal analysis of samples ageing for 180 days.

#### 4. Conclusions

During the ageing paste of magnesia, microsilica and water the first expected product of phase evolution should be brucite, but only the DTA-TGA-EGA analysis indicate on present of brucite in studied paste. This is probably due to simultaneous, the formation of brucite and very fast conversion it in to MSH phase. In case of pastes ageing for longer time, starts crystallize hydrated phases. The DTA-TGA-EGA analysis revealed broad effect around 400°C up to 650°C and second effect around 850°C, for samples ageing over 10 days at 20°C, that can be interpreted as decomposition of hydrated phases, it can be concluded that it is probably poorly crystalline magnesium silicates.

#### Acknowledgment

This work is supported by the grant no UDA-POIG.04.04.00-18-010/09-00 of the Polish Government.

#### Reference

- [1] Amaral L F R, Oliveira I, Bonadia P, Salomão R, Pandolfelli V C 2011 Chelants to inhibit magnesia (MgO) hydration *Ceramic International* **37** 1537-1542
- [2] Salomão R, Bittencourt L R M, Pandolfelli V C 2007 A novel approach for magnesia hydration assessment in refractory castables *Ceramic International* **33** 803-810
- [3] Kitamura A, Onizuka K, Tanaka K 1995 Hydration characteristics of magnesia *Taikabutsu Overseas* **16** 3-11
- [4] Salomão R, Pandolfelli V C 2007 Microsilica addition as an antihydration technique for magnesia-containing refractory castables *The Bulletin of the American Ceramic Society* **86** (2007) 9301-9309