www.czasopisma.pan.pl PAN www.journals.pan.pl

ARCHIVES
of
FOUNDRY ENGINEERING

DOI: 10.24425/123609

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

ISSN (2299-2944)
Volume 18
Issue 3/2018

95 – 100

17/3

# Analysis of Slag Activity on Corrosion of Ceramic Materials in a Slurry Furnace

**M. Wędrychowicz [a, *], A.W. Bydałek [b], B. Basiura [c]**

[a] Faculty of Mechanical Engineering, University of Zielona Gora, ul. Prof. Z. Szafrana 4, 65-516 Zielona Góra, Poland
[b] Faculty of Non-Ferrous Metals, AGH University of Science and Technology, al. Mickiewicza30, 30-059 Kraków, Poland
[c] KGHM Polish Copper inc., Legnica Copper Smelter and Rafinery, ul. Złotoryjska 194, 56-220 Legnica, Poland
* Corresponding author e-mail adress: maciej.wedrychowicz@gmail.com

Received 09.05.2018; accepted in revised form 23.07.2018

## Abstract

The article discusses the process of copper production in a slurry furnace and in a converter, with the indication of corrosion effects of the extractor. The furnace shaft and settling furnace of the flash furnace were analyzed. The basic factors determining the choice of single-stage technology of copper smelting in relation to the exploitation of refractory materials were indicated. The effects of dissolving the furnace lining material through slag have been presented. Structural analysis results using a scanning microscope are also included. The kinetics of destruction of ceramic materials under the influence of copper slag were evaluated. It has been shown that detailed analyzes are necessary in order to extend the time of furnace extensibility of furnaces in copper processes. The surface layer of the crucible softens due to saturation with slag reagents and is then washed out and moves in the solid form to the slag. The research in the article indicate not only the possibility of dissolution of the ceramic material in the molten slag, but also possibility of erosive activity of the slag on that material.

**Keywords:** Furnace lining, Ceramic material, Refractory corrosion, Flash furnace slag, Copper

## 1. Introduction

In the first stage of its development the process production of copper was based on the technology of the Finnish company Outokumpu Oy, whose process focused on obtaining copper matte and copper-nickel matte from chalcopyrite concentrate. At the stage of improving the efficiency of the process based on Finnish technology it was noticed that Polish Copper Concentrates have a low contents iron up to 4% and sulphur up to 13%, which allowed for the introduction of a single-stage copper smelting process, meaning without the operation of conversion of the copper matte used in the Outokumpu technology.
To change in the nature of the application of the Outokumpu technology contributed high contents of organic carbon. For the first time the single-stage process for obtaining copper was launched at HM Głogow II on 8 January 1978. Due to the strict EU rules on $CO_2$ emissions both at the moment, HM Głogow I and the modernized HM Głogow II are based on the single-stage process of obtaining copper. The meaning of this research is to find the answer, what kind of material should be used in the flash smelting furnance. In order to find the best solution of material, the test of erosive effect of the slag on a ceramic material (made of $Al_2O_3$) was carried out.

## 2. Analysis of the issue

Obtaining copper based on smelting of copper matte from pyrite concentrates according to the classic Outokumpu technology was characterized by low heat losses due to the using the heart of the flash furnace of multiple layers of insulation and its insufficient cooling. Allowed such a solution for obtaining

preventing the secretion of a thick layer of magnetite and more favorable energy performance of the process.
The slag from Polish concentrates contains a significant amount of cuprous oxide and copper, which have direct contact with the refractory lining, therefore the conditions of a single-stage process are entirely different. Such a chemical composition, the slag in relation to the furnace refractory lining is aggressive, well in the current technology there is no durable protective layer, which could ensure the continuity of the production process over a period of several decades. The purpose of the research is to demonstrate the chemical interaction of the slurry slag with the refractory material made of aluminium oxide.

## 2.1. Technological process

Figure 1. shows the technological diagram of the process of obtaining copper at HM Głogow II.

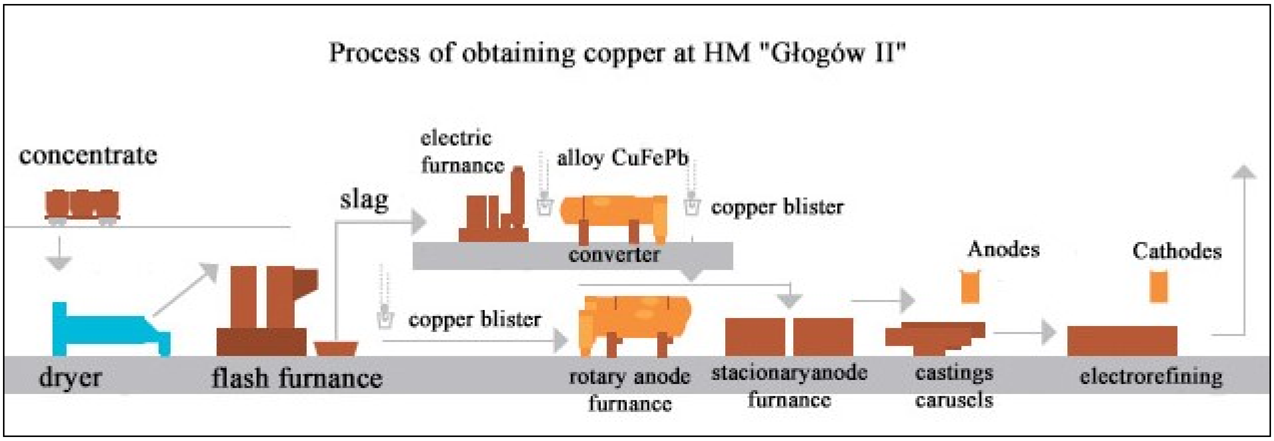

Fig. 1. Diagram of the process of obtaining copper at HM Głogow II [1]

Derived from Ore Concentration Plant Polkowice and Ore Concentration Plant Rudna the mineralogical concentrate is subjected to processes, which are name referred to as preparatory operations and include [2]:

a) drying (the concentrate is drying to a level of 0.3% $H_2O$),
b) selection concentrate and grinding concentrate (the dried to granules with a size over 0.75 mm).

The dry charge is transported to the feed tank with a pneumatic conveyor and is then tank fed by four concentrate burners into the reaction shaft of the flash furnace. in the reaction shaft of the flash furnace occur exothermic reactions of oxidation of sulphides and reactions between the oxide and the copper sulphide occur in the settler, in accordance with reaction (1) [3].

$$2Cu_2O + Cu_2S = 6Cu + SO_2 \quad (1)$$

To the reaction shaft of the flash furnace supplied is presents in Fig. 2. The copper from the anode furnace in the subsequent stages is poured to the rotary casting machine, and then subjected to the process of electrorefining in settlers. As a result using electrolysis, the purification copper with a purity exceeding 99.9% is obtained [4,5]. From the flash furnace slag is directed into an electric furnace where an alloy of iron, lead and copper is obtained. This alloy in subsequent production stages is directed to the Hoboken converter, and then to the anode furnaces.

The decoppered waste slag is granulated, and following the carbon monoxide are the burning to $CO_2$ from the electric furnace the process gases are cooled and dedusted in the pulse bag filter [6].

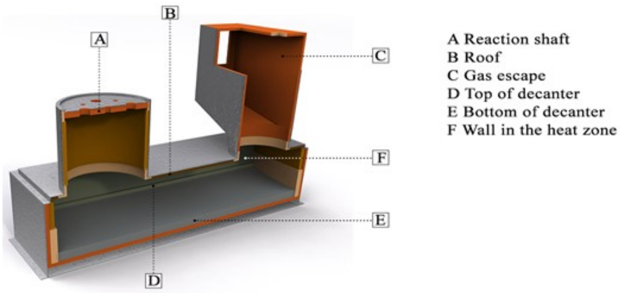

Fig. 2. Flash furnace from direct to blister process [8]

## 2.2 Operating conditions

In the metallurgical industry despite the large differences in the construction furnaces of used melting cooper in each of them we can notice the presence of four generally destructive impacts, which include:

1) high temperature,
2) thermal stresses,
3) mechanical impact,
4) corrosive effect of the slag.

In Fig. 3 is present the diagram of the behavior of the refractory walls of the furnace in conditions of strong heatin . In accordance with the prevailing temperature gradient a magnesium-chromite refractory shape heated from one side will expand under the influence of heat .

As a result the expansion of the shape and limited by the adjacent shapes will be crack and deform [10]. Stresses will increase in the adjacent fittings and move over the entire wall surface causing further cracking in the furnace lining. The impact of charge dusts and the abrasive motion of the moving charge in the furnace also will result in the deformation of furnace linings, for example in the form of the ovalization of the cooling shell it is the corrosive effect of the slag is however the most important. The corrosion processes may penetrate to the inside of the furnace walls or occur on the surface of the refractory lining. Process gases, because they have the highest penetration ability, mainly under the influence of $SO_2$ and $SO_3$ also will contribute to this corrosion.

The most vulnerable to corrosion areas are located in the molten slag district. The most aggressive slag reactants include: hydrogen and hydrocarbons, carbon monoxide, oxygen, sulfur oxide and vanadium oxide along with zinc and lead compounds. In addition, carbon monoxide undergoes thermal decomposition into carbon dioxide and carbon in the temperature range of 500°C to 600°C [5]. Result from decomposition builds up in the interior of the furnace lining fixed carbon and the carbon, blowing it up from the inside. In addition, present in the slag the iron oxides can undergo so-called inversion, i.e. pass from the oxide phase to the spinel phase, and these reactions are accompanied by uneven changes in volume of the slag which in turn leads to layered flaking and cracking of the walls.

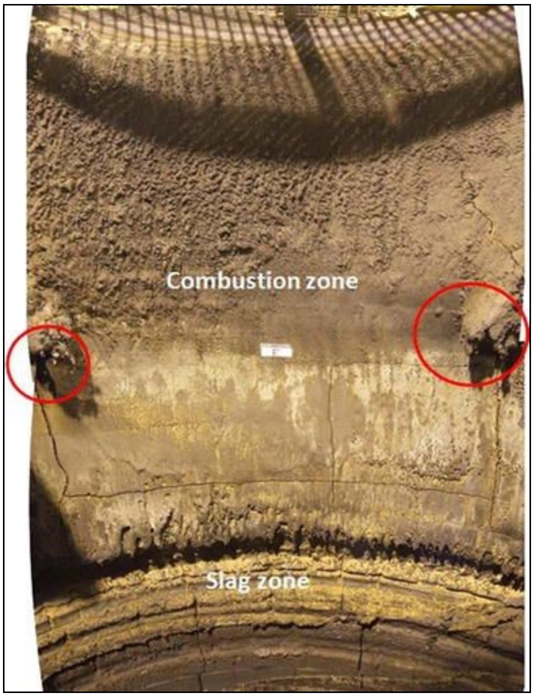

Fig. 3. View of the combustion and slag zone at the eastern furnace side. Severe corrosion of the refractory in the slag zone. Formation of massive build ups at the lance ports (circles) [9]

The Lower Silesian Magnesite Plants supply the products for the flash furnace for the Głogow II Copper Smelter. Mainly are these two magnesite products: CM3 and MC5-20. The chemical composition of the products (an example) manufactured at The Lower Silesian Magnesite Plants is presents Table 1.

Table 1.
Chemical composition of the products used in copper metallurgy [11]

| | Chemical Composition [%] | | | | | |
|---|---|---|---|---|---|---|
| Manufacture | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | $Cr_2O_3$ | CaO | MgO |
| CM3 | 4,0 | 12,4 | 12,6 | 33,0 | 0,6 | 35,0 |
| MC5-20 | 2,0 | 7,0 | 4,0 | 17,0 | – | 62,0 |

## 3. Determination of the impact of slurry slag on the refractory material lining

### 3.1. Research plan

The purpose of the research is to demonstrate of the slurry slag (the chemical interaction) with the refractory material made of aluminium oxide. The slag from direct to blister process obtained from Glogow copper smelter was first grinding in a vibratory crusher and then selection of fractions under 0.1 mm was placed in a ceramic corundum crucible in the amount of about 80g. After that shredded slag was melted in the temperature range from 1200°C to 1380°C in a resistance furnace. After the removal of the studied sample and cooling of the slag the crucible was broken and its fracture was studied macroscopically and microscopically. Conventional scanning electron microscope was used to imaging slag particles in operating vacuum. For this purpose cross sections of examined samples where at first hot mounted in conductive resin and polished with a use of diamond suspension. Microstructure images where taken on Hitachi SU-70 microscope with BSE detector.

### 3.2. Results of the conducted research

This research is to find the answer, what kind of material should be use in the flash smelting furnace. The slag of obtaining smelting copper (from the single-stage process), but also the process gases and the dusts are characterized by high chemical aggressiveness towards the lining of the flash furnace [3]. In contrast with the classical Outokumpu technology and in according to the KGHM monograph, the slurry slag containing about 14% $Cu_2O$ and having direct contact with the flash furnace lining causes the deformation of the furnace hearth and the rapid wear of ceramic (materials refractory). A test of the effect of the chemical slurry slag on a ceramic material made of $Al_2O_3$ was carried out (in order to confirm the erosive effect of the slag). Figures 4 and 5 presents a macroscopic image of the slurry slag penetrating into the corundum crucible, whereas Figures 6 and 7 presents an image from a scanning microscope.

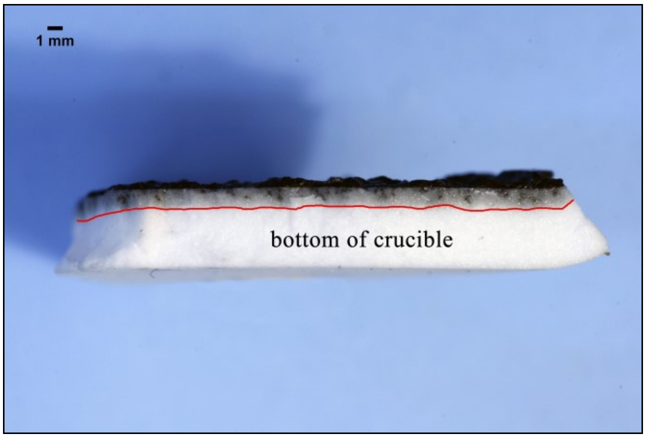


Fig. 4. View from the side of the corundum crucible after the measurement of slurry slag at 1360°C (natural size)

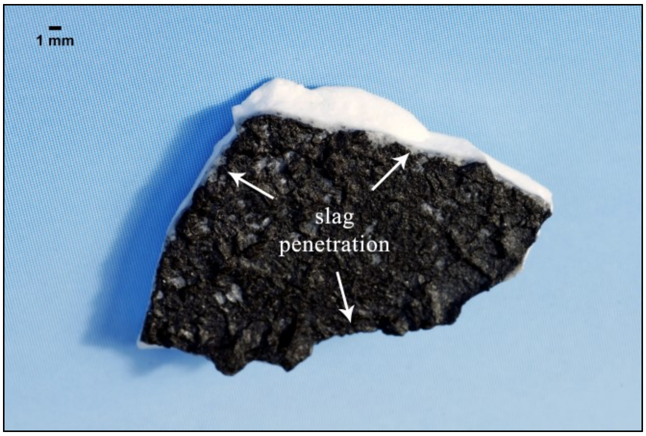


Fig. 5. View from the top of the corundum crucible after the measurement of slurry slag at 1360°C (natural size)

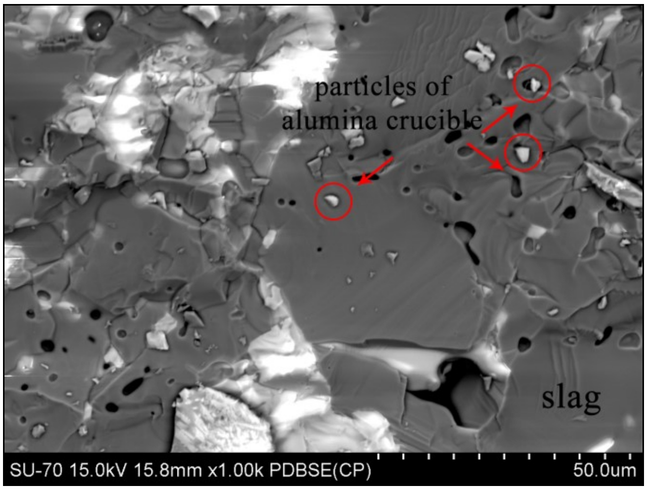


Fig. 6. SEM picture of the corundum crucible after the measurements

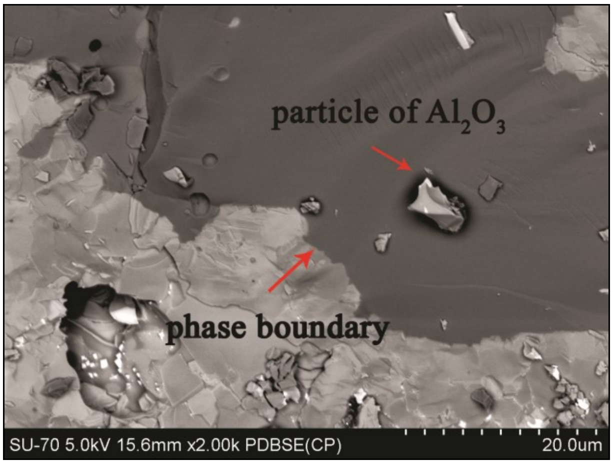


Fig. 7. SEM picture of the corundum crucible in different side of the crucible

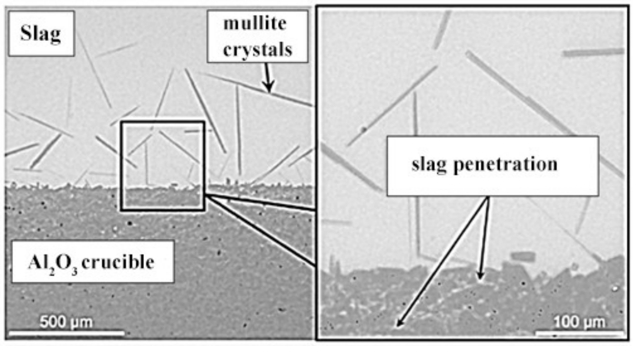


Fig. 8. SEM picture of mullite "niddles" formation

The results macroscopic and microscopic analysis indicate clearly the dissolution of the crucible material by the slurry slag and the movement of the slag - crucible phase boundaries deeper into the slag. According to one of the authors [12,13] this dissolution begins at the temperature of 1360°C (likely) with solid phase separations (hardly visible) in the form of mullite $Al_6Si_2O_{13}$. The phases mullite are present in the form of "needles" and their length (mainly) depends on the slag cooling rate. The faster the cooling, the size of the "needles" are the larger. During the dissolution of the material, small pieces of $Al_2O_3$ pass to the slag and is outlined in the crucible separating a clear boundary the slag from the aluminum oxide. Penetrating deeper, the surface of the aluminum oxide fills the slag which can be seen in Fig. 6. The mullite formation reaction at the $Al_2O_3$ – $Al_6Si_2O_{13}$ interface can be written as:

$$18Si^{4+} + 39Al_2O_3 \rightarrow 24Al^{3+} + 9Al_6Si_2O_{13} \quad (2)$$

Here, 39 moles of $Al_2O_3$ react with 18 moles of $Si^{4+}$ ions to form 9 moles of $Al_6Si_2O_{13}$. Mullite and mullite ceramics presents a great importance in both traditional and advanced ceramics. This is mainly due to its properties such as high thermal stability and favorable properties as conductivity and low thermal expansion, along with good mechanical strength and fracture toughness

[14,15,16]. Figure 9 presents phase diagram for the alumina – silica system.

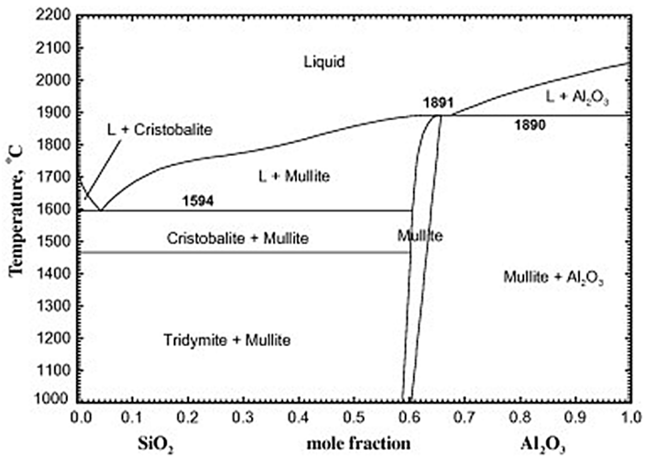


Fig. 9. Phase diagram for the alumina – silica system [17]

We notice a significant increase in the rate of dissolution of the ceramic material in the slag raising the temperature of the slag to 1380°C. In accordance with the $SiO_2$ – $Al_2O_3$ balance proceeds the formation of mullite in a very narrow chemical composition range, which indicate may that at temperatures lower than 1360°C chemical corrosion may occur through the slag components [18]. The surface layer of the crucible softens due to saturation with slag reagents and is then washed out and moves in the solid form to the slag.

## 4. Conclusion

In all types of flash furnaces among the least durable elements of the furnace is the furnace reaction area and it is decisive in its renovation cycles. Their durability does not exceed 10 months, despite the use of the best refractory materials in this area. The research in the article indicate not only the possibility of dissolution of the ceramic material in the molten slag, but also on the possibility of erosive activity of the slag on that material. Therefore, it is important to conduct further works and research on the development of refractory materials which will allow for extending the cycle of works between the renovations of the flash furnace.

## Acknowledgements

This project was supported by the National Center for Research and Development under Grant No. PBS3/A5/45/2015 (PBS3/244 864/PP/MMB).

## References

[1] KGHM Polish Copper inc. (2008, April), *Głogow Copper Smelter*. Retrieved May 5, 2001, from http://student.agh.edu.pl/~sitg/wyjazdy/kghm_2006/HMG_2008. pdf.

[2] Kucharski, M. (1987). Effect of Thermodynamic and Physical Properties of Flash Smelting Slags on Copper Losses During Slag Cleaning In an Electric Furnace. *Archives of Metallurgy*. 32(2), 259-262.

[3] Czarnecki, J., Śmieszek, Z. & Milczkowski, Z. (2001). The process of fluidized-bed furnace slag-cleaning and Cu Pb Fe alloy converting at Głogów II copper smelter. *Rudy i Metale Nieżelazne*. 46(5-6), 221-227. (in Polish).

[4] Villarroel, D. (1999). Process for refining copper in solid state. *Minerals Engineering*. 12(4), 405-414.

[5] Bydałek, A.W., Bydałek, A., Wołczyński, W. & Biernat, S. (2015). The concept for the process of slag decopperisation in the flash furnace process use the complex reagents. *Archives of Metallurgy and Materials*. 60(1), 319-322.

[6] Gargul, J., Pluciński, S., Warmuz, M. et al. (1994). Technology of blister copper production in a flash furnace at the Głogow copper smelter – achievements and prospects for the development. *Rudy i Metale Nieżelazne*. 39(11), 322-326. (in Polish).

[7] Bydałek, A.W. (2011). Role of carbon In the melting copper processes. *Archives of Foundry Engineering*. 11(spec.3), 37-42.

[8] Elliott J.F. (1976). Phase Relationships in the Pyrometallurgy of Copper. *Metallurgical Transactions B*. 7b, 17-33.

[9] Gregurek, D., Wenzl, C., Kreuzer, A. et al. (2016). Refractory Corrosion Mechanisms in a Novel High Carbon Ferromanganese Production Furnace. *Journal of the Minerals, Metals and Materials Society*. 68(12), 3029-3039. ISSN: 1047- 4838.

[10] Pirowski, Z. (2014). Evaluation of high temperature Physico-chemical Interactions Between the H282 Alloy Melt and Ceramic Material of the Crucible. *Archive of Foundry Engineering*. 14(4), 83-90.

[11] Elsner, M. & Ząbek, E. (1981). Refractory alkaline materials in the copper metallurgy and reasons for their consumption. *Materiały ogniotrwałe*. 4, 107-113. (in Polish).

[12] Zhu, J., Kaneko, T.K., Mu, H. et al. (2012). Effects of Measurement Materials and Oxygen Partial Pressure on Synthetic Coal Slag Viscosity Values, MOLTEN12: ninth international conference on Molten slags, fluxes and salts, Beijing, China, 27–31 May 2012 (pp. 1 – 16). Conference materials, electronic document.

[13] Wędrychowicz, M., Kucharski, M. (2013). Viscosity variation of the slag from direct to blister process during its de - coppering. Recycling of non ferrous metals-international conference 6–8 February 2013 (pp. 42) Cracow. (in Polish).

[14] Schneider, H., Komarneni, S. (2006). *Mullite*. (1st edition). Springer Link. John Wiley and Sons. ISBN: 978-0-387-73361-6

[15] Schneider, H., Schreuer, J. & Hildmann, B. (2008). Structure and properties of mullite – a review. *Journal of the European Ceramic Society*. 28(2), 329-344.

[16] Anggono, J. (2003). Mullite Ceramics: Its Properties, Structure, and Synthesis. *Journal Teknik Mesin*. 7(1), 1-10.
[17] Klug, F.J. & Prohazka, S. (1987). Alumina – silica chase diagram in the mullite region. *Journal American Ceramic Society*. 70, 750-759.
[18] Walton, M.C. (2013). Refractories 101. *Ceramic Industries magazine*. 1, 1-5.