

Worn Refractory Bricks – Alko: Resource of Corundum and Mullite Clinkers

B. Plešingerová, P. Vadász, E. Dedinská, J. Derďák, D. Chudíková

Determination of the recycling possibilities of worn materials obtained from Alko 80 AMC-S and Alko 60 A refractory bricks is the aim of this work. The spent linings from the pouring ladle for pig iron transport and steel ladle were investigated. The quality and composition of the particle-size classes were evaluated after crushing of the spent linings. The degree of contamination of refractory masses, the redistribution of the fundamental components (Al_2O_3 , MgO , SiO_2 , C) into grain fractions of (0–1 mm), (1–2,5 mm) and (2,5–5 mm) and magnetic proportion were observed. The iron particles and Fe- and Ca-compounds are mainly concentrated in the magnetic proportion. 70–75 mass-% of refractory material from spent Alko 80 AMC-S bricks could be effectively recycled. It is possible to obtain the size class of 1–5 mm with content up to 80–85 % of Al_2O_3 . The redistribution into size classes during the crushing of the spent Alko 60 A bricks did not occur. After removing the magnetic fraction, the residue contains more than 95 % of $(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ with the dominant mullite phase.

fine-grain matrix – binding materials and antioxidants, eventually. The fine particles cover the clinker grains and are filling the voids between the grains. The components react together under a high temperature, the high-temperature solid-phase reactions occur and new amorphous and crystalline phases are formed.

Moreover, during the high-temperature metallurgical processes the refractory materials in units fall into the mutual interactions, the interaction with the molten metal, slags and gaseous phases. The chemical reactions, together with the physical and mechanical actions, can disturb the integrity of the heat-resistant material. The aggressive molten metal attacks the surface part of the bricks strongly, the metal slowly infiltrates into the pores of the refractory material and the individual grains are gradually released into the melt. The volume changes, the differences in the material dilatation of components cause the mechanical damage under the sintered surface layer of refractory material, which speeds up the process of lining degradation. The load conditions (high temperatures and repeated cycles, convection of melts and their aggressiveness), but mainly the refractory quality (composition and density/porosity) determine the period of service of the exposed lining. In the most cases the sharp boundary between attacked surface layer and lining core is created. Often, only a very narrow surface layer is strongly corroded by molten metal. The bulk of the core lining is not deteriorated so much as it is on the surface. The substantial part of refractory material applied in this part of ladle which is in contact with metal (“metal zone”) is chemically almost unchanged. Nevertheless, the long term exposure of refractory materials to high temperatures can develop the phase transformations, the formation of stable high temperature phases [9–12]. The presented work is focused on the recovery of alumina heat-resistant material

Beatrice Plešingerová, Pavol Vadász,
Eva Dedinská
Technical University of Košice
Faculty of Materials, Metallurgy and
Recycling
Institute of Metallurgy
042 00 Košice
Slovakia

Ján Derďák, Daša Chudíková
R.M.S. a.s.
042 00 Košice
Slovakia

Corresponding author: B. Plešingerová
E-mail: beatrice.plesingerova@tukesk

Keywords: recovery, post-mortem refractory material, alumina silicate

Paper presented at REFRA 2017 in Prague

1 Introduction

The steel producers are among the largest consumers of high-alumina refractory materials. The linings of high-temperature metallurgical units, such as pouring ladle for pig iron and ladle for secondary metallurgy technologies of steel (e.g. deoxidation, doping and others), are formed from alumina ceramic bricks. These are applied in zones where the linings are in contact with the molten metal. These materials are attacked by molten metal under the temperatures of more than 1600 °C over long periods and cyclically exposed to the thermal shocks and extreme stress, to what they should be resistant [1–3].

The cost of high-quality ceramic raw materials is high and therefore the ceramic refractory manufacturers are looking for ways of recycling the materials from the worn refractory linings [4–9].

Refractory masses are composed of the clinkers of the different particle size and

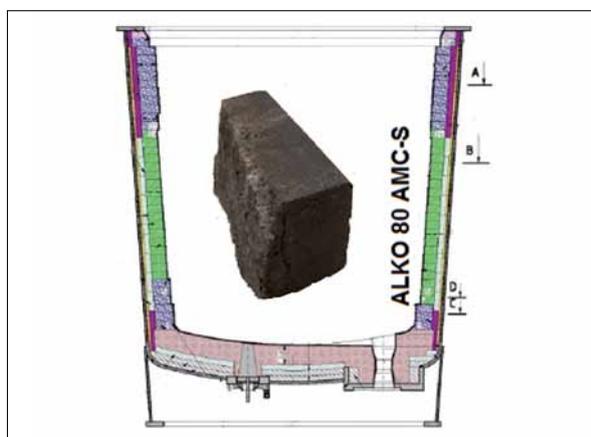


Fig. 1 Steel ladle for secondary metallurgy, application: the working lining of wall which is in direct contact with the molten steel

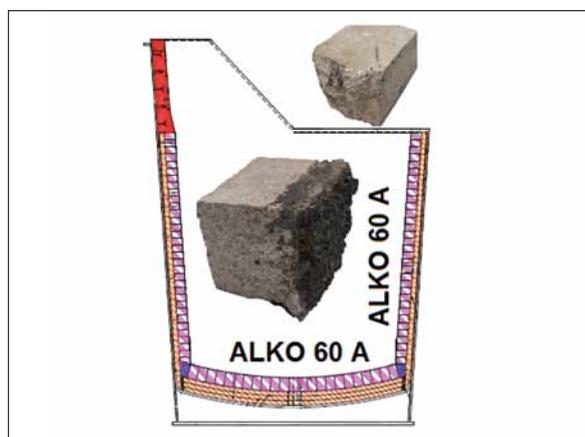


Fig. 2 Pouring ladle for pig iron, application: lining of the bottom and the walls; bricks from zone under and above slag line

obtained from two kinds of worn bricks: Alko 60 A and Alko 80 AMC-S, which have been applied into pouring ladle for pig iron transport and steel ladle for secondary metallurgy. R.M.S. a.s. Košice, DZ REFRAKO/SK is a producer of these refractory bricks. The aim was to evaluate the possibilities of reusing the part of worn material as raw material for the production new refractory bricks and/or creation of gunning material.

2 Experimental

The worn Alko 80 AMC-S bricks were taken from a steel ladle for secondary metallurgy after 198 casting runs (Fig. 1), and worn Alko 60 A bricks from a pouring ladle for pig iron transport after 521 casting runs (Fig. 2).

The Alko 80 AMC-S refractory bricks are bauxite-based with the organic bound, which has high resistance to liquid metal and therefore it is used as a working lining of steel ladles. This material is in direct contact with molten steel and resists up to a temperature of 1700 °C.

The chemical composition of mass is as follows: 78 mass-% Al_2O_3 , min. 6,5 % MgO, min. 5 % C, max. 1,2 % Fe_2O_3 and approx 2,3 % SiO_2 . The bricks show the apparent porosity of 8 % and density of min. $2950 \text{ kg}\cdot\text{m}^{-3}$ [13].

The Alko 60 A bricks are andaluzite-based and they are applied up to 1650 °C. Material shows the tensile strength of min. 55 MPa, density of min. $2440 \text{ kg}\cdot\text{m}^{-3}$ and the increased resistance to the liquid metal and molten glass, therefore it is used as a lining of pig iron ladles in intensively stressed zones [14].

The surface of the bricks from the steel ladle (Fig. 1) and pouring ladle for pig iron (Fig. 2) was greatly worn and disrupted in a thin layer of about 5–15 mm. Therefore, the material from the surface was separated (layer thickness approx 20–25 mm) from the core of brick and evaluated separately. The materials were crushed into grain size under 5 mm gradually and sieved to three factions (0–1 mm; 1–2,5 mm and 2,5–5 mm) that were quantified. The magnetic particles were separated by the magnetic separation and the conventional methods were applied to determine the chemical composition of all grain fractions. The results of the analysis are listed in Figs. 3, 4. Several selected samples were characterized by X-ray diffraction analysis (Rigaku MiniFlex 600). The diffraction records were evaluated using the quality analysis software PDXL 2 and ICDD mineral and ceramics database. All the diffraction lines in the records were allocated to phases and the main lines of the phases are marked (Figs. 3, 4).

3 Results and discussion

Approximately 40–55 vol.-% of refractory material from the ladle lining is spent during the working cycles, this material passes into the slags. The rest of the Alko 80 AMC-S lining in a ladle represents about 5–8 t of worn materials. The sintered surface layer of the bricks with very thin accretion is only a few millimetres thick. In the case of the Alko 60 A bricks, the molten metal leaks into cracks which are located several millimetres under the sintered surface and probably these cracks primarily generate the thermal shocks during the pouring period.

The refractory materials under the surface layer look as unused bricks.

It is difficult to separate the sintered corroded surface layer from the less corroded core material. The weight ratio of the surface material comparing to the core material depends on how thick coating was separated. It affects the results of the chemical analyses of the crushed samples. Manually sorted worn lining from the steel ladles and the pouring ladle for pig iron were gradually crushed and re-sieved, and the magnetic particles were put aside. Qualitatively different classes were obtained by the consequent separation of crushed non-magnetic material into size fractions: 0–1 mm; 1–2,5 mm and 2,5–5 mm.

The chemical composition of the strongly corroded surface and core bricks are presented in Fig. 3 and Fig. 4. It points out to the differences in degree of the brick contamination and the distribution of components into size fractions.

Alko 80 AMC – S: The mass proportion of the (0–1 mm), (1–2,5 mm), (2,5–5 mm) fractions and the Al_2O_3 , SiO_2 , Fe_2O_3 , CaO, MgO, TiO_2 and C (as loss by ignition) contents are presented in Fig. 3.

Alkali metal oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) content in the samples obtained from the corroded surface was less than 0,3 mass-%, and sulphur content was not in a detectable amount.

Of course, the magnetic part contains the highest proportion of Fe – compound and the total magnetic proportion obtained from the crushed bricks is 3–4 mass-%.

In our case, the weight ratio of the material from surface and core was 1 : 9. It is

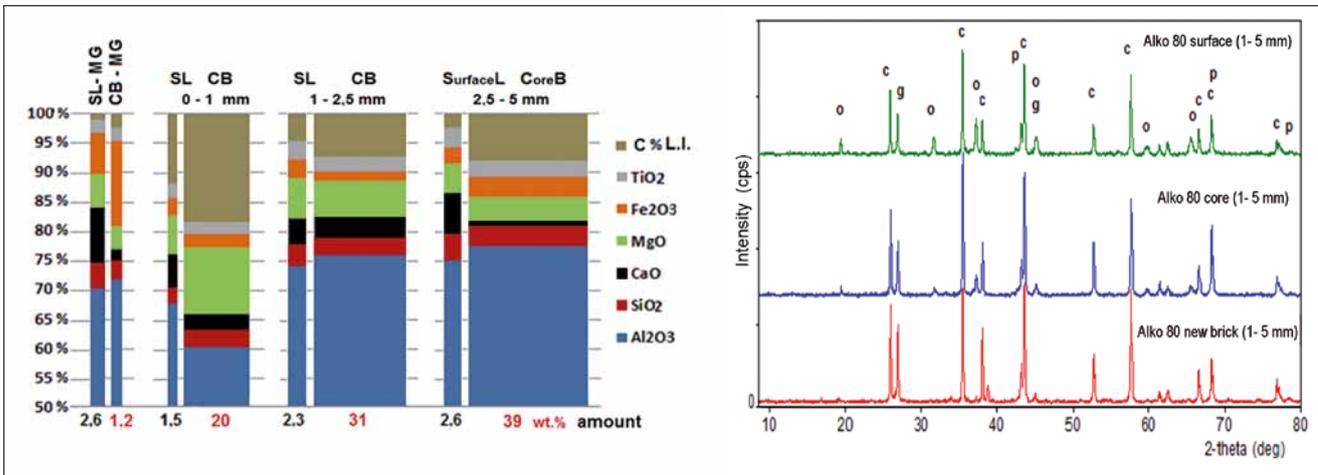


Fig. 3 Alko 80 AMC-S:

- redistribution of components into grain fractions from worn bricks (material from SL – surface layer; CB – core brick, MG – magnetic part), L.I. – loss on ignition;
- X-ray patterns of 1–5 mm fraction of sample from new and worn bricks: c – corundum (Al₂O₃); g – graphite (C); p – periclase (MgO), o – spinel (MgAl₂O₄)

obvious from the results of analyses that Al₂O₃ is accumulated in coarser fractions (1–2,5 mm and 2,5–5 mm) but MgO and C in fine fraction (0–1 mm). The phase composition of worn refractory materials was compared with the material from the new brick. The results are shown in Tab. 1.

Strongly attacked surface layer of bricks represents a small portion of the worn bricks. Relatively high-quality Al₂O₃ clinkers of 1–5 mm granularity can be obtained by crushing of the bricks after the simple magnetic separation. 75 mass-% from spent bricks forms the size class of 1–5 mm, which contains more than 76 % of Al₂O₃. If carbon from this fraction burn up, the Al₂O₃ content increases approx to 85 mass-%. Carbon oxidation from finer fraction (0–1 mm) with higher C content increases the Al₂O₃ content from ~60 mass-% to ~75 mass-%.

ALKO 60 A: The weight proportion of obtained size fractions (0–1 mm; 1–2,5 mm and 2,5–5 mm) from worn Alko 60 A bricks and their chemical composition is shown in Fig. 4. The content of alkali metal

oxides (Na₂O + K₂O) in the samples from surface layer achieved the value lower than 0,25 mass-% and the sulphur was detected only in trace amount. Despite of the cracks filled with metal under the great corroded surface layer, the separation of this surface layer from core brick is difficult. The magnetic weight proportion obtained from the crushed surface brick, which were in direct contact with molten iron, was 14–18 mass-%, but after recalculating to the whole brick it makes 4–5 mass-% only.

The significant difference between the finer and coarser classes, after separating the magnetic particles, was not found. Crushing does not lead to the redistribution of the components into size classes. Perhaps only a note: The CaO content in the 0–1 mm fraction from the surface of the bricks was higher (2–3 mass-%). The major content of Al₂O₃ and SiO₂ in all non-magnetic fractions corresponds to andalusite/sillimanite ratio (Al₂O₃·SiO₂ = 63 : 37). Although the examined spent bricks from pouring ladle for pig

iron from the zones above and under slag line have the chemical compositions comparable, the phase analyses indicated that probably that was the case of two kinds of bricks (Tab. 2). The mullite phase was detected as dominant in the worn bricks from the zone above slag line, which were free of accretion. Besides mullite, there was a small amount of the sillimanite identified, too. In the case of the worn bricks with Fe-accretion, the diffraction lines of mullite along with the andalusite were identified.

4 Conclusion

The key factor of reusing worn refractory materials from spent lining is a manual sorting immediately during the ladle lining demolition. Unlike the pouring ladle for pig iron, which is made of one type of material, the lining in each zone of steel ladle is formed by different refractory materials, which are often different in chemistry, but they are visually similar.

The analysis of worn Al₂O₃-refractory bricks from pouring ladles and steel ladles showed that, after the gradual crushing of the manually sorted worn bricks into particle size of less than 5 mm, the most contaminated parts of lining materials can be removed by magnetic separation. The types of crushing machines determine the quantity of obtained fractions.

In the case of Alko 80 AMC-S, the fine-grained fraction (<1 mm) is enriched

Tab. 1 Comparison of phase proportion in grain fractions of Alko 80 AMC-S bricks

Phases	Alko 80 AMC-S Bricks for Steel Ladle; Fraction 1–5 mm [mass-%]		
	Surface	Core	New brick
Corundum	55–63	62–73	65–78
Graphite – carbon	11	9	11
Titanium oxide	6–5	4–5	1–2
MA-spinel	20	6–9	traces
Periclase	5–9	8	10

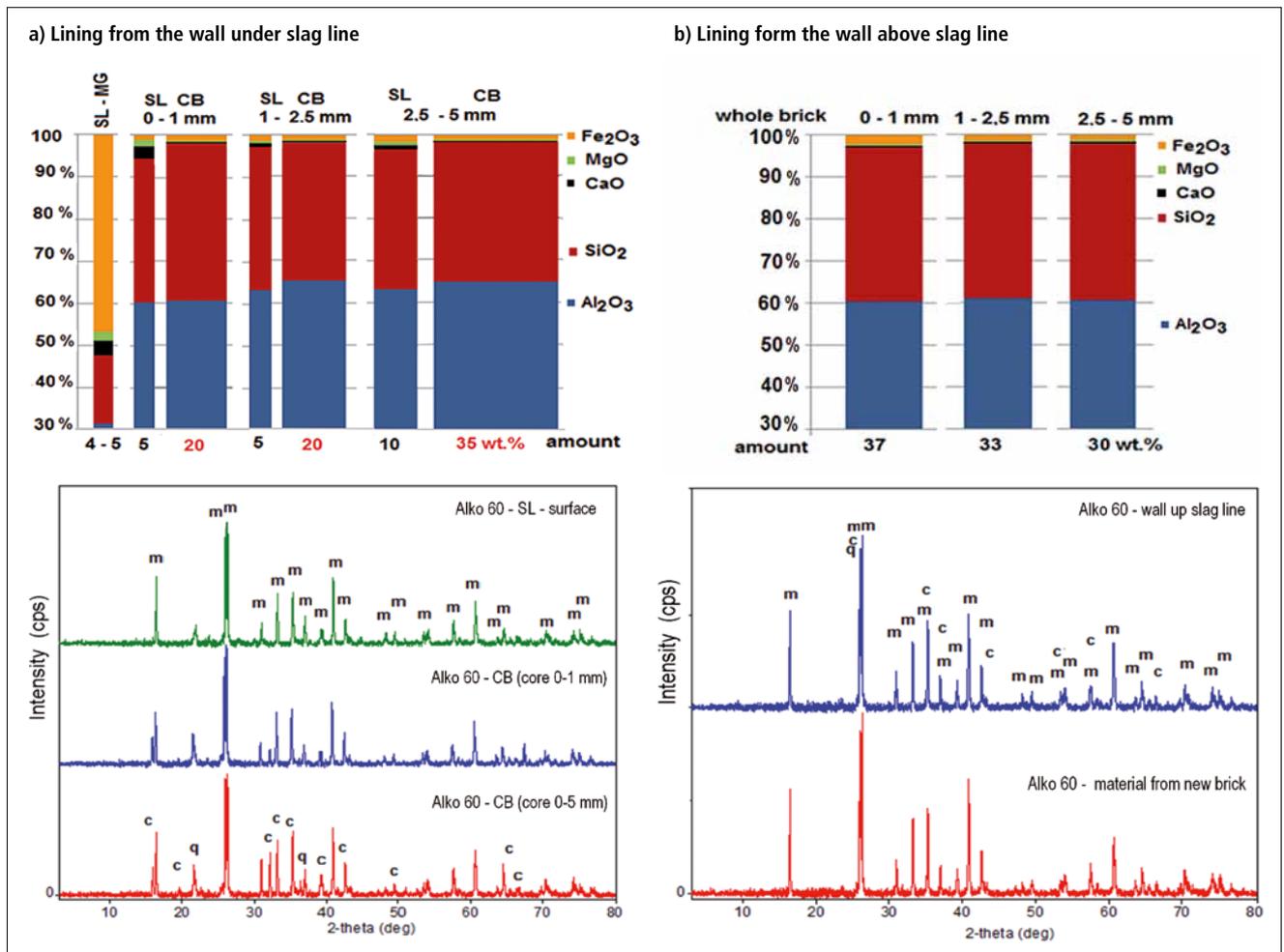


Fig. 4 Alko 60 A, bricks from zones: a) under, and b) above slag line:
 • redistribution of components into grain fractions from worn bricks (material from SL – surface layer; CB – core brick, MG – magnetic part);
 • X-ray patterns of sample from new and worn bricks: c – corundum (Al_2O_3); m – mullite ($3Al_2O_3 \cdot SiO_2$); q – cristobalite (SiO_2)

with carbon and MgO, and the corundum clinker is accumulated in the coarser fraction. The 1–5 mm size class contains more than 75 mass-% of Al_2O_3 and is less contaminated with spinel phase. This material can be used without further treatments for Alko AMC refractory materials production. If carbon is removed by ignition, the Al_2O_3 content increases (~85 mass-% Al_2O_3). The non-carbon fine class (0–1 mm) could be utilized as additive in gunning mixtures. The 75–80 mass-% of materials from this spent lining could be returned back into production as good-quality refractory raw material.

In the case of the Alko 60 A, the accretions from the surface of corroded bricks, which are mainly magnetic ones, can be removed by magnetic separation after the crushing. After the magnetic particles removal

the chemical composition of the residual crushed fractions (0–1 mm, 1–2,5 mm and 2,5–5 mm) occurred as almost iden-

tical. Based on the detected differences in the phase composition of the linings from the wall under and above the slag line we

Tab. 2 Comparison of phase proportion in grain fractions of Alko 60 A bricks

Phases	Alko 60 A Bricks for Pouring Ladle for Pig Iron, Fractions [mass %]				
	Under Slag Line (Direct Contact with Iron)		Above Slag Line		
	Core (0–5 mm)	Core (0–1 mm)	Surface (0–5 mm)	Core (1–5 mm)	New brick (1–5 mm)
Corundum	8	5–7	1–3	4–7	4–6
Sillimanite	–	–	–	92	93
Mullite	76–79	75–79	89	–	–
Andalusite	5–7	5–7	trace	–	–
Cristobalite	3–5	4–5	~2	~1	~1
Calcium, magnesium, iron, silicon oxide	traces	2–3	3–5	–	–

presume that in pouring ladle were applied two kinds of Alko bricks in these zones. Probably, the used bricks were produced from different $\text{Al}_2\text{O}_3\text{-SiO}_2$ – raw materials (sillimanite/andalusite).

The fractions contain (60–64) mass-% and (30–34) mass-% of Al_2O_3 and SiO_2 , respectively. Mullite creates dominant phase. Approximately 90 mass-% of this spent material, of relatively good quality, can be reused in the production as the refractory raw materials.

Acknowledgement

This publication is the result of implementation of the project "Research Excellence Centre on Earth's sources extracting and treatment (Project No. 26220120017)" supported by the Research & Development Operational Program funded by the ERDF.

References

[1] Chudíková, D.; et.al.: Vymurovka oceliarskej panvy z materiálov z produkcie spoločnosti RMS a.s. Košice. In.: Oceláři. Konference 4.–

5.4 Karlova Studánka (2013)
 [2] Munoz, V.; et.al.: Thermal evolution of $\text{Al}_2\text{O}_3\text{-MgO-C}$ refractories. In.: 11th Int. Congr. on Metallurgy & Materials SAM/CONAMET 2011. Procedia Mater. Sci. (2012) [1] 410–417
 [3] Chen, L.; et.al.: Degradation mechanisms of alumina-silica runner refractories by carbon steel during ingot casting process. Ceramics Int. **42** (2016) [8] 10209–10214
 [4] Schutte, M.: Refractory recycling earning your environmental brownie points. In: The Southern African Institute of Mining and Metallurgy Refractories Confer. (2010) 75–85
 [5] Nakamura, Y.; et.al.: Recycling of refractories in the steel industry. Industrial Ceramics. **19** (1999) [2] 111–114
 [6] Ferreira, G.; et. al.: Environmental analysis for identifying challenges to recover used reinforced refractories in industrial furnaces. J. of Cleaner Production **88** (2015) [2] 242–253
 [7] Hanagiri, S.; et.al.: Recent improvement of recycling technology for refractories. In: Nippon steel technical report **98** (2008) 93–98

[8] Richter, F.; Nemčok J.: Využívání speciálních druhotných surovin. In: Suroviny 2015, Silikátová společnost České republiky z.s. (2015) 1–3
 [9] Malenšek, N.; et.al.: Recycled granulates obtained from waste alumina-rich refractory powder by the cold bonding process. Ceramics Int. **41** (2015) 8996–9002
 [10] Yang, J.-Z.; et. al.: Solid particle impact erosion of alumina based refractories at elevated temperatures. J. of the Europ. Ceramic Soc. **32** (2012) [2] 283–289
 [11] Nadachwski, F.; Kloska, A.: Refractory wear processes. AGH Krakow (1997) 133
 [12] Jansson, S.; et. al.: Corrosion mechanism and kinetic behaviour of refractory materials in contact with $\text{CaO-Al}_2\text{O}_3\text{-MgO-SiO}_2$ slags. In. Int. Confer. „Molten Slags Fluxes and Salts“. The South African Institute of Mining and Metallurgy (2004) 341–347
 [13] Classification of dense shaped refractory products. Part 4: Special products, STN EN 12475 – 4. 2001
 [14] Classification of dense shaped refractory products. Part 1: Alumina-silica, STN EN 10081 – 1. 2003

Publication Schedule 2018

Issue	Central Themes	ED	AD	PD	Additional Circulation on Following Events
1	Raw materials; secondary raw materials; energy efficiency; refractories for cement and glass; refractories for steel and non-ferrous metals	06.12.17	24.01.18	18.02.18	IREFCON; New Dehli/IN; 07.-09.03.2018 IMFORMED Mineral Recycling Forum ACerS Refractories Section; St. Louis/US; 21.-22.03.2018 Glassman Latin America; Guadalajara/MX; 21.-22.03.2018 ceramitec 2018; Munich/DE; 10.-13.04.2018 Int. Conf. for Refractory Makers and Metallurgists; Moscow/RU; 19.-20.04.2018 Global CemProcess; London/GB AISTech; Philadelphia/US; 07.-10.05.2018 IMFORMED MagForum
I	refractories HOT TOPICS			14.03.18	newsletter preview AISTech, ACerS Refractories Section
2	Refractories for glass and ceramics; waste incineration; power generation; petrochemistry; foundries; aluminium; steel	02.03.18	27.03.18	26.04.18	Aluminium Middle East; Dubai/UA; May 2018 IFAT; Munich/DE; 14.-18.05.2018 Metal + Metallurgy China; Beijing/CN; 16.-19.05.2018 Global Slag; Dusseldorf/DE Metef; Verona/IT DGG; Bayreuth/DE; 28.-30.05.2018 Made in Steel; Milano/IT; June 2018
II	refractories HOT TOPICS			09.06.18	newsletter preview Int. Colloquium on Refractories
3	Refractories for iron and steel; foundries; raw materials; recycling-green manufacturing; aluminium Special: Int. Colloquium on Refractories Aachen	21.06.18	25.07.18	28.08.18	Glassman Europe; Lyon/FR Aluexcon; Mumbai/IN Minerals, Metals, Metallurgy; New Dehli/IN; 29.-31.08.2018 Ankiros; Istanbul/TR; 20.-22.09.2018 Int. Colloquium on Refractories; Aachen/DE; 26.-27.09.2018 Fundi Expo; Guadalajara/MX; 24.-26.10.2018
III	refractories HOT TOPICS			03.09.18	newsletter preview Aluminium and glasstec
4	Refractories for aluminium; glass; non-ferrous metals; cement; waste incineration; green refractories Special: Aluminium and glasstec 2018	10.08.18	05.09.18	01.10.18	Aluminium; Dusseldorf/DE; 09.-11.10.2018 glasstec; Dusseldorf/DE; 23.-26.10.2018 Heat Treat; Columbus/US Iran Metafo; Tehran/IR
IV	refractories HOT TOPICS			04.12.18	newsletter preview 2019 (GIFA; METEC; THERMPROCESS)