INGOT FEEDING SYSTEMS

ANALYSIS OF FIBERS' BEHAVIOUR BEFORE/AFTER CASTING

2nd International Conference ICRF 2014

Authors	
Fabio Sola	JODOVI S.r.l – Via Lombardia 9 – 21015 Lonate Pozzolo (VA) - Italy
Davide Mombelli	Dipartimento di Meccanica, Politecnico di Milano , via La Masa 1, 20156 Milano, Italy
Carlo Mapelli	

ABSTRACT

During the cooling and solidification of castings in foundry or ingots in steel plant, the metal shows a certain volume reduction called "shrinkage". To avoid shrinkage porosities it is necessary to supply additional molten metal contained into a special reservoir: the feeder head. To optimize feeding performances are commonly used chemical products called "feeding aids", such as special covering powders and linings for the feeding cavity walls, usually called "sleeves" or "feeder heads". After the cooling, when the metal shape is extracted, the linings are crumbled and workers can be exposed to the originated dusts. These linings are prefabricated products and every producer has its proprietary formulation; some of them contain Refractory Ceramic Fibers (RCFs), special wools with outstanding insulating properties, that have been included even into a list of substances at very high concern due to their carcinogenicity. On the other hand, other formulations may contain different fibrous materials such as mineral wools (MW) that are chemically different and represent a health-friendly alternative to RCFs.

Through in-field trials, the possibility to achieve satisfactory solutions by RCF-free products was investigated. The morphological and the chemical transformations occurring in these products after the exposure to molten steel during the casting operations were also investigated through the comparison between the products before and after the casting. Comparisons with RCF-containing products were also performed. The obtained results highlighted that the replacement of traditional products containing ceramic fibers with RCF-free alternatives guarantees the same metallurgical quality of the products with a significant improvement of the health that can be assured in the workplace.

KEYWORDS

Refractory Ceramic Fibers, Carcinogenic, Foundry Aids, Lining, Riser, Feeder, Sleeve, Ingot, Casting.

INTRODUCTION

During the solidification of a steel casting a volume contraction always takes place. In order to avoid shrinkage cavities caused by this volume contractions, or to move them far from the areas interested by plastic deformation processes, extra molten metal must be provided and this operation implies feeding the casting by molten steel. Several products (called "feeding aids") are available, and they were specifically developed for this aim: side wall linings, also called "sleeves" or "feeder heads", anti-piping powders and topping compounds used to insulate the top of the open risers from the atmosphere [1]. These products have several benefits:

- reduction of heat transfer rate between mold and riser;
- increase of effective modulus of a riser;
- reduction of liquid metal needed to produce a given casting;
- cost saving.

In this study, different class of feeding aids products were investigated, namely the sleeves used in foundry and the side wall linings used in steel plant.

These products may contain Man-Made Vitreous Fibers (MMVFs), included into the family of Man-Made Mineral Fibers (MMMFs, Fig. 1). According to EC Directive, MMVFs are divided in “Refractory Ceramic Fibers” (RCFs) and “Mineral Wools” (MWs): MWs are defined as man-made vitreous (silicate) fibers with random orientation, characterized by alkaline and alkaline-earth oxides ($Na_2O+K_2O+CaO+MgO+BaO$) content greater than 18% by weight; RCFs are defined as man-made vitreous (silicate) fibers with random orientation, containing alkaline- and alkaline-earth-oxides ($Na_2O+K_2O+CaO+MgO+BaO$) less or equal to 18% by weight.

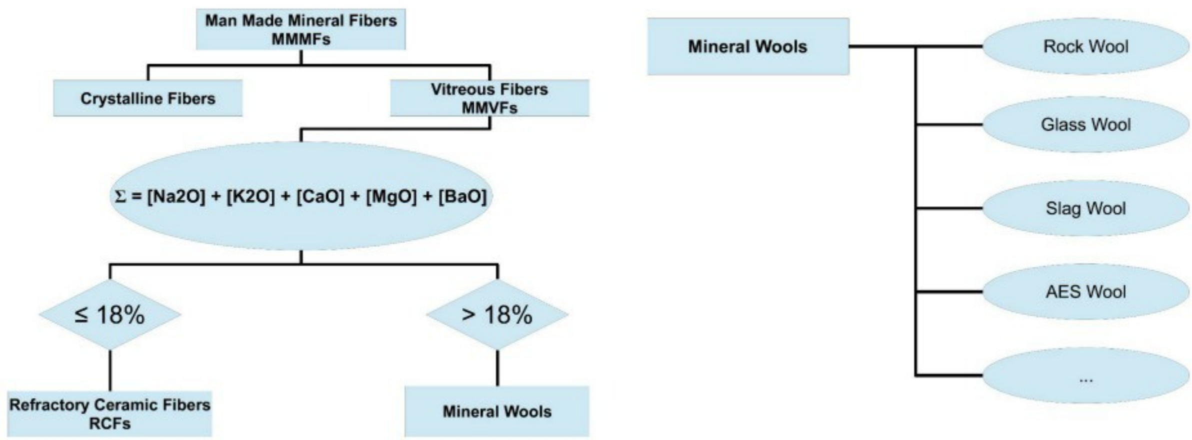


Fig 1: Classification of Man-Made Minerals FIbers

Rock, slag, glass wool and alkaline-earth silicates (AES) wool belong to the family of mineral wools.

Glass wool is produced on a spinning cup from silica sand, soda ash dolomite, limestone, ulexite and anhydrite, and contains a higher fraction of alkaline oxides than alkaline-earth oxides. Rock wool is produced on a cascade spinner from basalt rocks, dolomite, limestone and coke and contains a higher fraction of alkaline-earth oxides than alkaline oxides; similar wools can be produced using iron-ore blast-furnace slag as partial replacement of the standard raw materials [2-4].

AES wool is a family of products commercialized since the Nineties of the 20th century, made from a mixture of calcium, magnesium, aluminum and silicon oxides [4,5]. In force of their chemical composition and morphology, these fibers are classified as potential carcinogenic or non-carcinogenic as a function of their typology. For example, the ACGIH classified rock wool fibers as animal carcinogen with unknown effects on humans (Group A3) [6]. In 2002, The IARC re-classified insulation glass wool, continuous glass filament, rock (stone) wool and slag wool from Group 2B (possible carcinogenic to humans) to Group 3 (not classifiable as to their carcinogenicity to humans) [4] whereas the European Regulation 1272/2008 included mineral wools in class 2 of carcinogenicity (suspected human carcinogen), but this classification decays when low biological persistence is proven ("Note Q") or when the fibers are not respirable ("Note R") [7]. Table 1 summarizes the carcinogenicity classes of mineral wools according to different health organizations.

MINERAL WOOLS			
Organization	**Canc. Class**	**Description**	**Year**
ACGIH	A3	Animal carcinogen with unknown effects on humans	2001
IARC	3	Not classifiable as to their carcinogenicity to humans	2002
EU	2	Suspected Human carcinogen	2008
EU	-	Not carcinogenic (Note Q, Note R)	2008

Table 1: Mineral Wools classifications.

RCFs are extensively used instead of asbestos in high temperature applications since the Seventies [8]. Two different raw materials can be exploited to obtain RCFs: the first is the kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), a natural aluminosilicate largely employed in several industrial application fields, the latter is a mixture of alumina (45-50%wt.) and silica (50-55%wt.) [9,10]. The raw materials are melt and the fibers are produced by blowing and spinning. However, during the production a certain fraction of the molten material (up to 50%) remains with shape of non-fibrous particle, conventionally identified as "shot" [8,9].

The end product is strong and has low density and excellent thermal shock resistance [11], leading to be used for several purposes such as the refractory lines and the insulating blankets of thermal treatment furnaces or the linings [8,10]. RCFs could be satisfactorily employed upon 1400 °C but when they are exposed to prolonged high temperatures, a phenomenon called devitrification may occur: the molecular structure changes from amorphous to crystalline [11], and although the insulating properties are not affected by this transition, the material becomes more brittle. Devitrification leads to the formation of mullite ($Al_6Si_2O_{13}$), cristobalite and other crystalline silica species [5,10,12-15]. In particular, cristobalite and the other crystalline silica species are classified as carcinogen by the IARC and several studies demonstrate that the employees of the metal industry are exposed to elevated airborne concentrations of respirable crystalline silica that can lead to respiratory effects, including silicosis and lung cancer [16-18].

Not only the devitrification products are dangerous for human health but also the unused RCFs. The Environmental Protection Agency (EPA) in 1993 classified RCFs in class B2, as probable human carcinogen [19]. One year later, the National Toxicology Program (NTP) classified respirable RCFs as "reasonably anticipated" to be a carcinogen; this classification is still in force in the 12th report of 2011 [20]. In 1997, RCFs were defined carcinogenic of category 2 ("May cause cancer by inhalation") and the definition is registered in the European Directive 97/69/EC [21]. Four years later (2001) the ACGIH classified RCFs as "A2 – Suspected Human Carcinogen" [6]. Only in 2002 the IARC declared a sufficient evidence of cancer in animals caused by inhalation of RCFs and, due to their high bio-persistence, classified RCFs in IARC group 2B (possibly carcinogenic to humans) [4]. In 2006 IARC also concluded that wool-like synthetic vitreous fibers may be respirable and the carcinogenic hazard can vary from high to low, with high for the bio-persistent fibers and low for non-biopersistent fibers [22]. Consequently, the European Chemical Agency (ECHA) included the RCFs in the "Substances of Very High Concern (SVHC)" list [23] and in the new revision of the European Regulation (1272/2008), RCFs are finally classified as 1B (may cause cancer by inhalation). This classification is also applied to mixtures containing RCFs as ingredients; the REACH stated that available information on alternative substances and techniques shall be provided, including information on the risks to human health and the environment related to the manufacture or use of the alternatives, availability, including the time scale, technical and economical feasibility [7]. Table 2 summarizes the carcinogenicity classes of the RCFs according to different international health organization. Citotoxicity and carcinogenicity of RCFs are then widely demonstrated by several author through various laboratory tests [24-27].

REFRACTORY CERAMIC FIBERS			
Organization	**Canc. Class**	**Description**	**Year**
EPA	B2	Data from animal studies sufficient to indicate potential carcinogenicity to humans	1993
ACGIH	A2	Suspected human carcinogen	2001
IARC	2B	Possibly carcinogenic to humans	2002
NTP	R	Reasonably anticipated to be human carcinogen	2005
EU	Cat. 1B	May cause cancer by inhalation	2008

Table 2: Refractory Ceramic Fibers classifications.

Mineral wools could represent a reliable alternative to RCFs for certain applications.

The most promising mineral wools are the AES wools that, as well as RCFs, are considered high temperature insulation wools (HTIW) and thus could be exploited for high temperature applications. This material, also named CSM is considered non-carcinogenic in force of its low bio-persistence. However, its maximum classification temperature is approximately 1200 °C in continuous operating systems [5] and when exposed to continued high temperature, AES wools tend to devitrify alike RCFs, producing crystalline silica species [12].

Other mineral wools, namely rock and glass wools, cannot ordinarily be used for high temperature applications (>800 °C) because of their low melting point; in addition, these fibers show high temperature transformations that don't lead to carcinogenic substances [3,12].

As soon as RCFs are classified as carcinogenic products and the available alternatives seem to not have the same technical properties, the development of new replacement material is imperative in order to assure occupational health safety and the same production quality, especially in the metal industry. Despite of several studies conducted on RCFs degradation after exposure to high temperatures, no literature regarding RCFs applications in the steel and foundry casting operations is available. The most of the scientific researches concentrated to the prediction of cristobalite formation in devitrificating ceramic fibers for prolonged high temperature exposure in a range between 1100 °C and 1350 °C [10,15,28-32], whereas other studies examined prolonged RCFs exposure to 1500 °C [13,14,33-35]. Anyhow, all the above mentioned investigations were performed through laboratory tests in quasi-static conditions. These experiments permitted to define a general trend about devitrification development: heating the fibers to very high temperature (over the recommended operational range) for short period leads to similar levels of devitrification as heating the fibers at low temperature for longer periods. This aspect is also compatible to the forecast offered by the Larson-Miller parameter: cristobalite is expected to form after 2 hours at the temperature of 1500 °C [14].

In this work, foundry sleeves and ingots side wall linings were prepared using refractory ceramic fibers. Their behavior after the exposure to the molten steel in ordinary working conditions was investigated. The comparison between traditional RCF-containing product and innovative RCF-free product was also performed from technical, morphological and chemical point of view. The reliability of RCF-free refractory was demonstrated from metallurgical quality of the obtained ingot and castings.

1 EXPERIMENTAL PROCEDURE

The comparison between standard RCF-containing products and innovative RCF-free ones was performed matching the quality and the metallurgical features of two equivalent components produced in the same batch exploiting two different types of products. The tests on field were carried out in two different industrial plants: a steelworks (case 1) and a steel foundry (case 2).

1.1 Case 1: Steelworks ingots casting

Two ingots P1100 of 15400 kg made of AISI 8630 steel were bottom cast at 1570 °C. Each ingot had a removable feeding head carrier, where the refractory linings were placed (Fig. 2). Just before the ingots started to cool down, during the filling of the feeder head, a certain amount of anti-piping powder was added. Two different lining products were adopted during the test: the first, labeled as s-1, is a traditional RCF fiber-supported product with subordinated particles (Fig. 2a); the latter, labeled as s-2, is an innovative particle-supported product with subordinated mineral wool fibers (Fig. 2b). The unused materials were characterized by SEM to determine the nature, the chemical composition and the morphology of the fibers. The RCF-containing products were also investigated by XRD to identify the crystallography nature of the fibers.

During the ingot stripping, burnt lining samples were collected immediately after the removal of the feeding head carriers. The burnt linings were examined again with the same techniques to detect possible chemical and morphological variations.

The ingot quality was determined by ultrasounds tests to characterize the distribution of the metallurgical defects.

(a) (b)

Fig 2: Arrangment of the refractory linings in the ingot feeder heads: (a) traditional RCF linings; (b) innovative linings.

1.2 Case 2: steel foundry casting

Two castings of a mechanical component of 28 kg by weight were made of ASTM A351 CF8M steel. The steel was poured at 1540 °C. The iso/eso sleeves were placed on the model and the molds were then filled by foundry sand (Fig. 3). After curing, on the molds and the cores the same foundry coating was applied and then all the parts were assembled for the casting. Immediately after the steel pouring, the risers are covered with the same covering powder. Two different lining (sleeves) were adopted during the test: the first, labeled as f-1, is a traditional RCF fiber-supported product with subordinated particles (Fig. 3a); the latter, labeled as f-2, is an innovative particle-supported product with subordinated mineral wool fibers (Fig. 3b). The unused materials were characterized by SEM to determine the nature, the chemical composition and the morphology of the fibers. The RCF-containing products were also investigated by XRD to identify the crystallography nature of the fibers.

The burnt lining samples were collected immediately after the castings were shakeout and sandblasted. The burnt linings were examined again with the same techniques to detect possible chemical and morphological variations. The casting quality was determined by visual test on the overall batch and the surface defects were determined by penetrating liquid control.

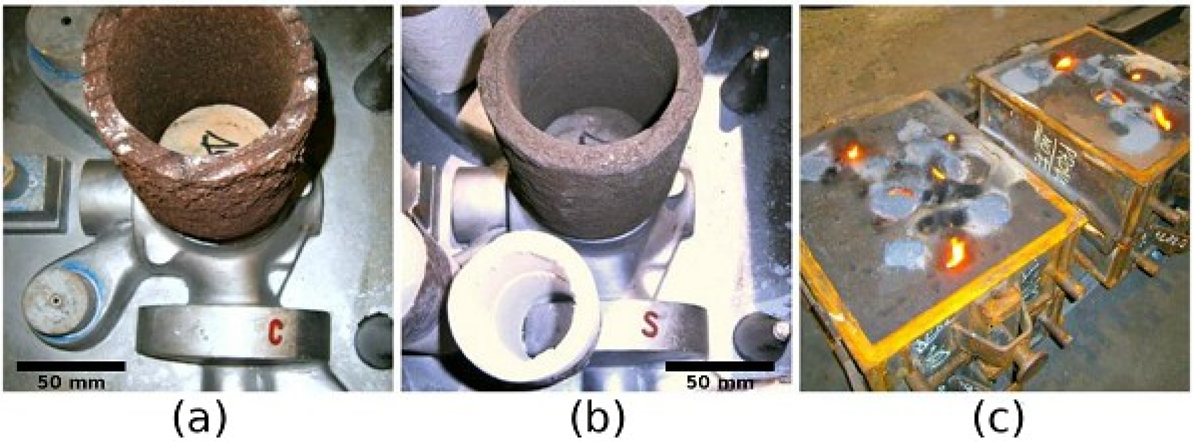


Fig 3: Arrangment of the refractory linings in the foundry models: (a) traditional RCF linings; (b) innovative linings; (c) moulds after casting operations.

1.3 Product characterization

Morphological and crystallographic characterization of both RCF-containing and RCF-free products before and after casting operations was performed by means of scanning electron microscopy and XRD analysis.

SEM analysis was carried out using both Jeol JSM 5500 LV (low vacuum) Scanning Electron Microscopy equipped with high resolution IXRF EDS 2000 micro-probe (20 kV, 10^{-11}A, 1 μm beam diameter) and Zeiss EVO50 Scanning Electron Microscope equipped with an Oxford Inca EDS probe.

X-ray diffraction (XRD) data was collected using a Philips PW3020 diffractometer in a θ-θ configuration and employing Cu Kα radiation (λ=1.54Å), scanning the sample between 10° and 80°. The samples were analyzed without grinding, to allow maintaining the fibers in the original form and shape. The qualitative analysis was performed with the Crystal Impact Match! software through the use of the Crystallographic Open Database (COD).

2 RESULTS

2.1 Case 1: steelworks ingots casting

SEM micrographies of the linings employed in the ingots casting are reported in Fig. 4.

Traditional RCF-containing linings (s-1) are characterized by typical fiber-supported structure (Fig. 4a). The fibers pointed out during morphological characterization can be attributed to refractory ceramic fibers; they are featured by an average diameters lower than 6 μm and a length-on-diameter ratio higher than 3 [21] (Fig. 4b). Moreover, their chemical composition (Fig. 4c) was compatible with that of RCFs, being constituted by an Al_2O_3/SiO_2 ratio close to 1. In addition, the fibers surface appeared smooth, with fracture perpendicular to the fiber axis and sometimes containing nodules, as reported by Gualtieri et al. [12].

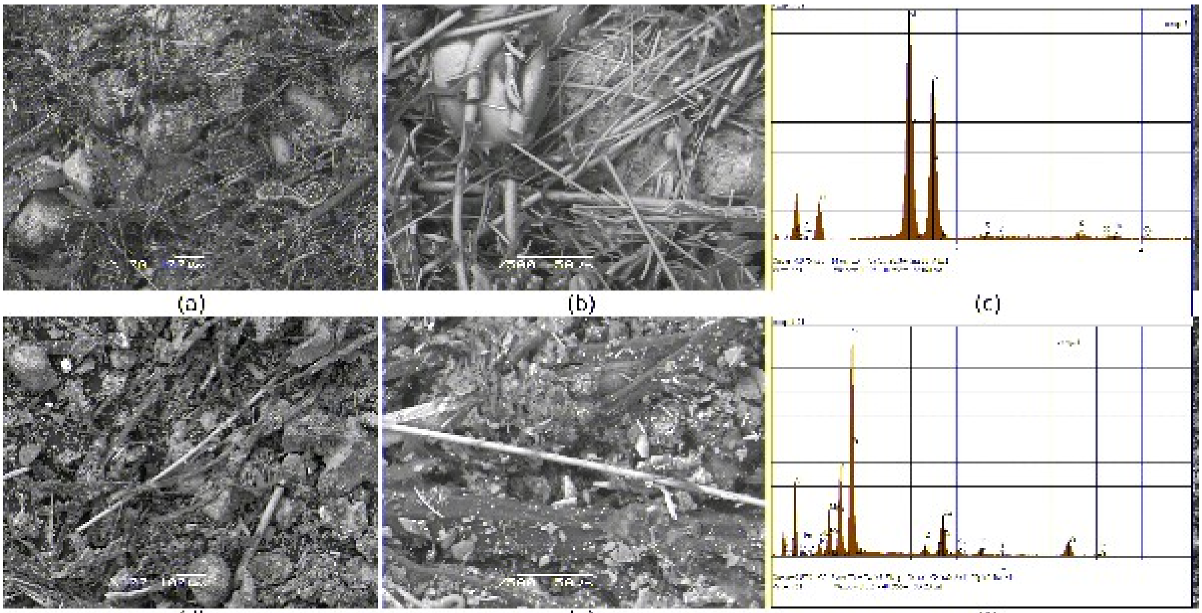


Fig 4: SEM micrographies and EDS spectrum of (a-c) RCF-containing refractory and (d-f) RCF-free refractory.

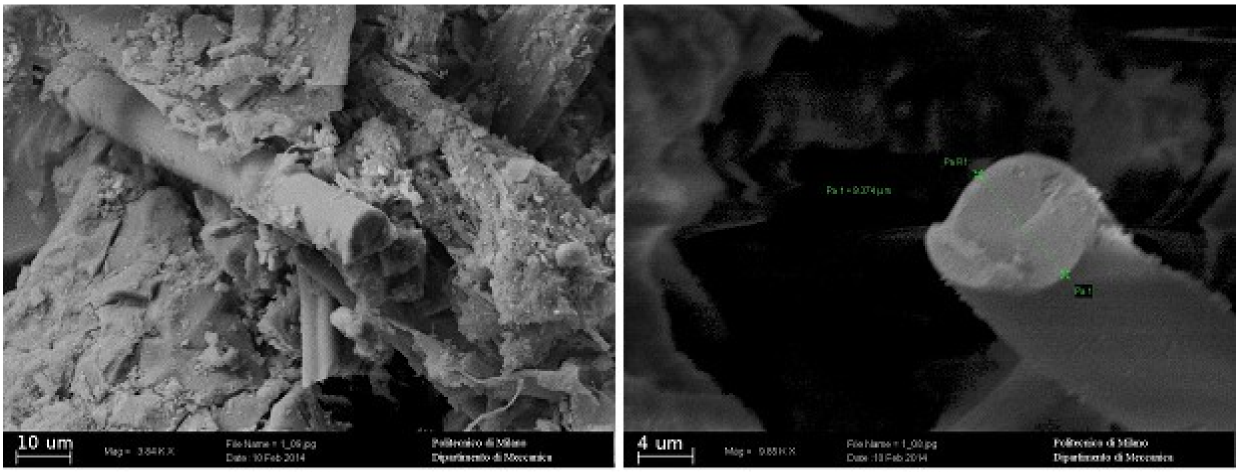


Fig 5: SEM micrographies at high magnification of the mineral wool fibers.

The samples taken from s-1 and s-2 were completely different: the SEM analysis confirmed the particle-supported structure of the RCF-free linings (Fig. 4d). Some fibers are detected but their size and their chemical composition are typical of mineral wools (Fig. 4e-f).

As soon as the summation of alkaline and alkaline-earth oxides is over than 18% by weight they can not be classified as carcinogenic. Moreover, the D_{LG}-2SE indicated in the EC regulation 1272/2008 (the average diameter weighed on the fiber length minus two times the standard error) for the mineral wool fibers contained int the RCF-free products is equal to 9.7 μm, thus larger than 6 μm, confirming their non-breathable behavior [7]. A detailed observation at high magnification of the fiber contained in the RCF-free linings is reported in Fig. 5. Thus, the new RCF-free refractory products completely fulfills the R and Q notes of European Regulation, therefore can be classified as non-carcinogenic material.

Test on-field to evaluate the performances of the proposed new RCF-free refractories is mandatory to demonstrate that the new formulation is technically equivalent (or even better) than the traditional but harmful products.

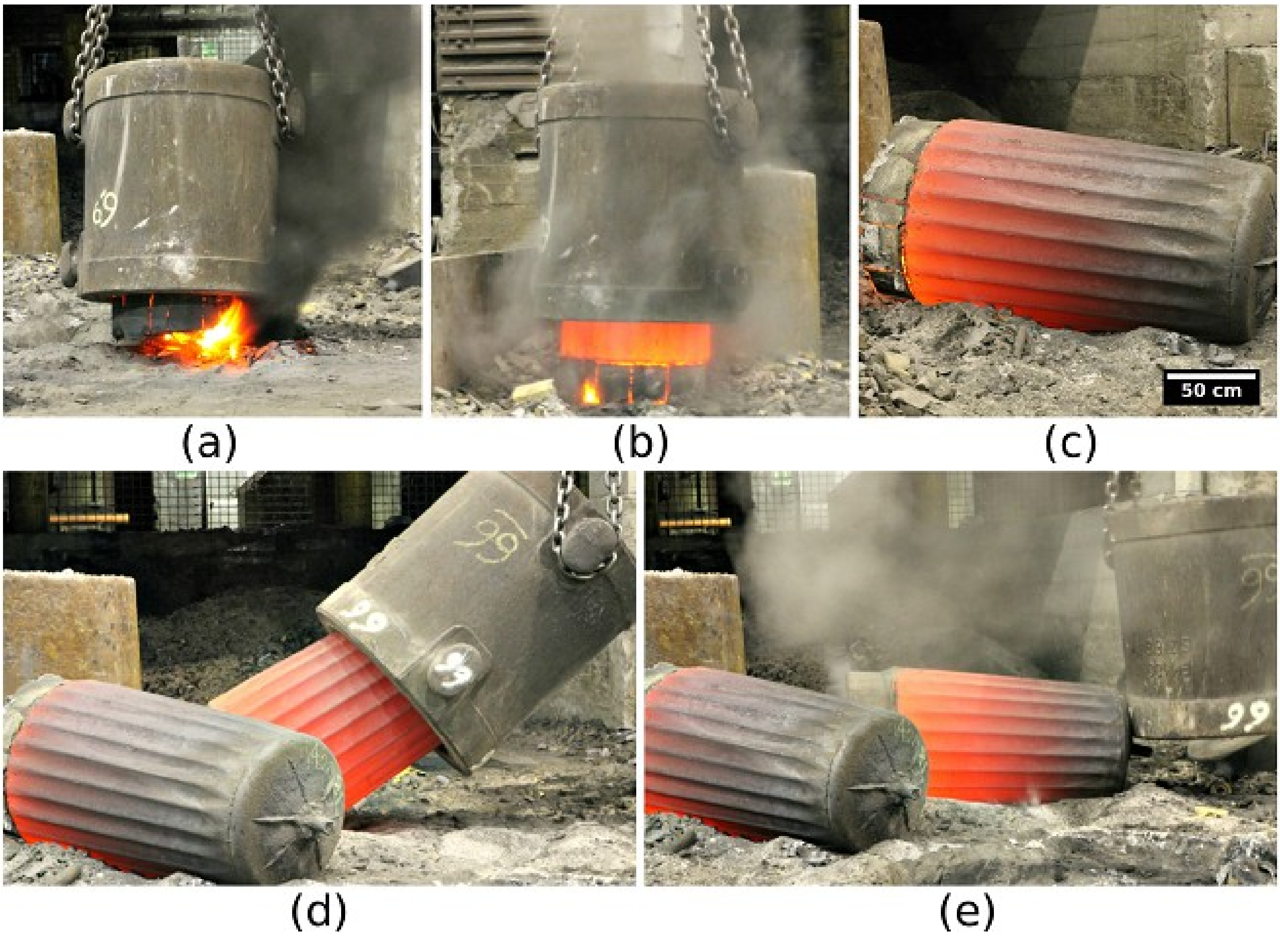


Fig 6: Pictures of investigated steel ingots: (a-b-c) RCF-containing linings ingot during the stripping operations; (d-e) RCF-free linings ingot during the stripping operations.

The ingot cast by RCF-containing linings was stripped at first (Fig. 6a). During the stripping operations, a large amount of powder was released into the environment (Fig. 6b). The high dustiness seems associated to the disintegration of the refractory linings when they fell on the floor. Figure 6c shows the ingot just after the mold removal. The ingot featured by RCF-free linings was stripped 10 minutes after the first (Fig. 6d). In this case, the dustiness produced during the stripping was less than in the previous case. Effectively, the s-1 products after the casting were crumbly, with a visible collapse of the support structure. On the contrary, the s-2 products remained compact with enough mechanical resistance to

avoid disintegration.
The thermal status of the cast ingots can be estimated by the observation of the color pointed out by the ingots. The ingot endowed with RCF-free linings seemed to be hotter then the first ingot. Actually, the extension of the hot zone of the second ingot (Fig. 6e) is wider than that of the first one (Fig. 6c). This aspect is a clear index of the better insulation of the hot-top, that allow to maintain hot the steel for a longer time.
After cleaning, the ingots were transfered to another department of the steel plant for further treatments. Both the ingots had a bowed shrinkage, but the ingot endowed with RCF-free linings is still hotter than the first one (Fig. 7).
Given that the RCF-free linings height was 4 cm smaller than the other, and since the ingot endowed with s-2 products resulted hotter than the traditional, a reduction of the overall molten steel to be cast should be possible. An initial estimation of material saving that could be achieved adopting RCF-free linings is approximately the 2% by weight, that in this case means roughly 300 kg of saved steel.

After the solidification and the cooling were fulfilled, both the ingots underwent the ultrasound inspection operated by skilled technicians compliant with the UNI EN 473 standards. Both the ingots resulted free from shrinkage cavities.

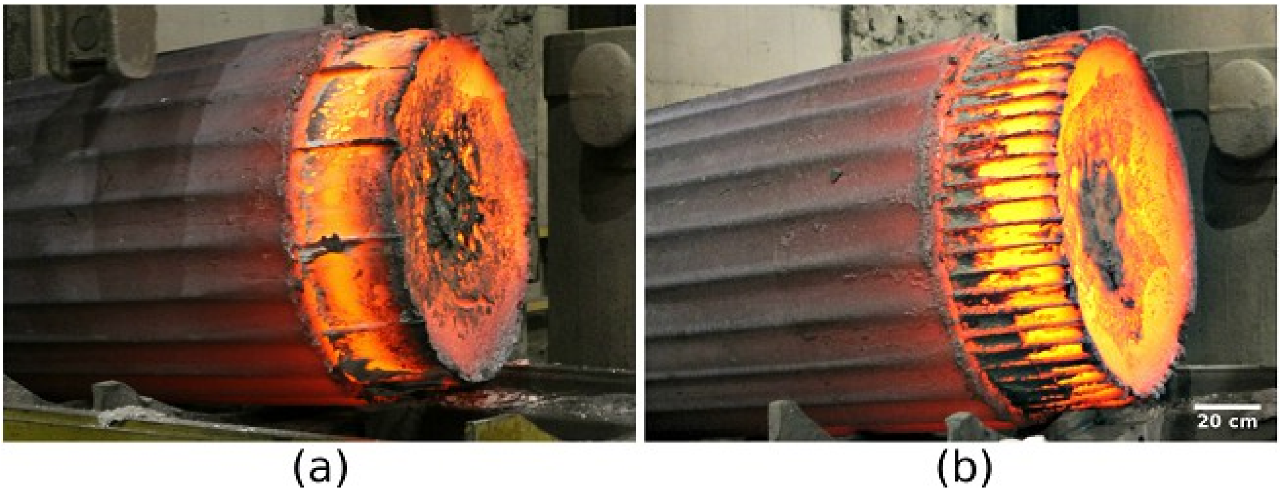


Fig 7: Ingots ready for the thermal treatments: (a) endowed with RCF-containing linings and (b) endowed with RCF-free linings.

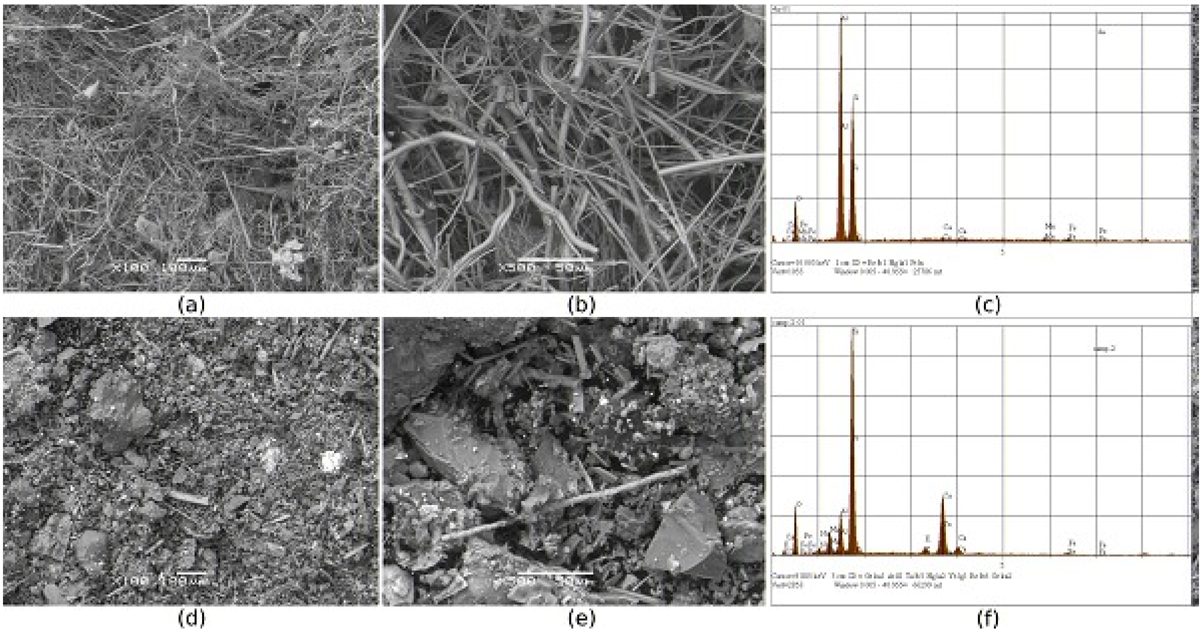
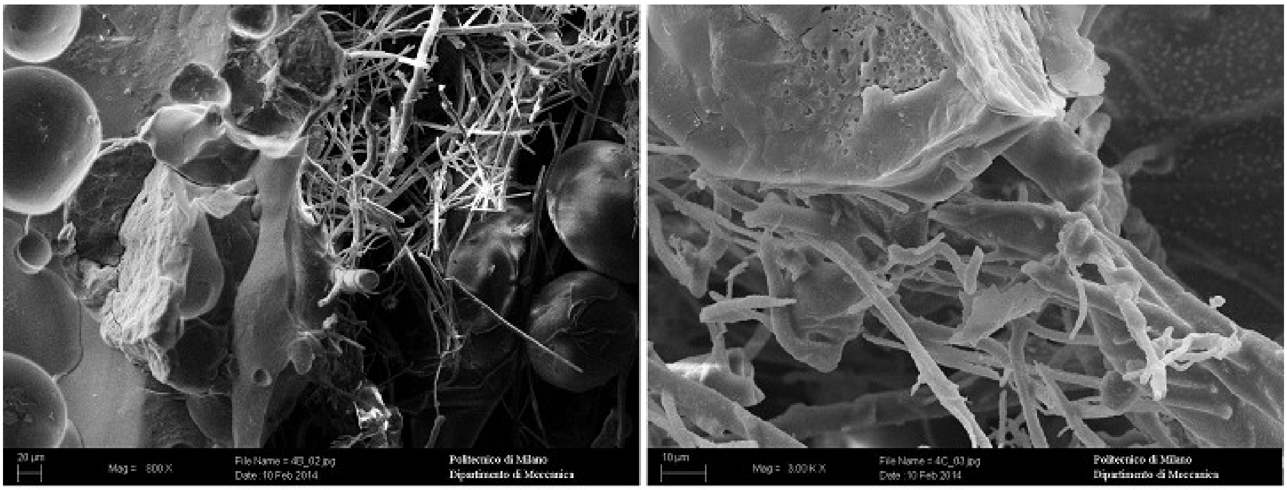


Fig 8: *SEM micrographies and EDS spectrum of (a-c) burnt RCF-containing refractory and (d-f) burnt RCF-free refractory.*

The burnt linings were then analyzed again by SEM and the RCF-containing linings also with XRD. Both the products (s-1 and s-2) have lost their binding system, becoming very brittle and crumbly. However, RCF-free products still kept a certain mechanical resistance to prevent complete pulverization.

The structure of s-1 linings (containing RCFs) was morphologically unchanged after use (fiber supported with subordinated particles) (Fig. 8a-b); also the fibers showed no morphological variation, but the measurement of their chemical composition pointed out the presence of Fe and Mn (Fig. 8c). These elements are certainly associated to the steel (or to the slag covering the rising steel). The slag is chemically aggressive and it could start to react with fibers changing their chemical composition. Analysis of the fiber-slag interfaces (Fig. 9) allowed visualizing the reaction between slag and fibers: parts of the fibers were embedded in the slag (Fig. 9a). Moreover, as visible in Fig. 9b, the exposure to the high temperature featuring the slag induced surface modifications on the RCFs: the fibers appeared rough and partially melted, with major broken fibers and nodules due to the coalescence between adjacent fibers (sintering process). In addiction the fiber diameters seemed to decrease, further increasing the breathability of such fibers.

JODOVIT S.r.l. - Chemical Group
Via Lombardia, 9 – 21015 Lonate Pozzolo
VARESE – Italia
Tel: +39 0331301086
mail@jodovit.com – www.jodovit.com

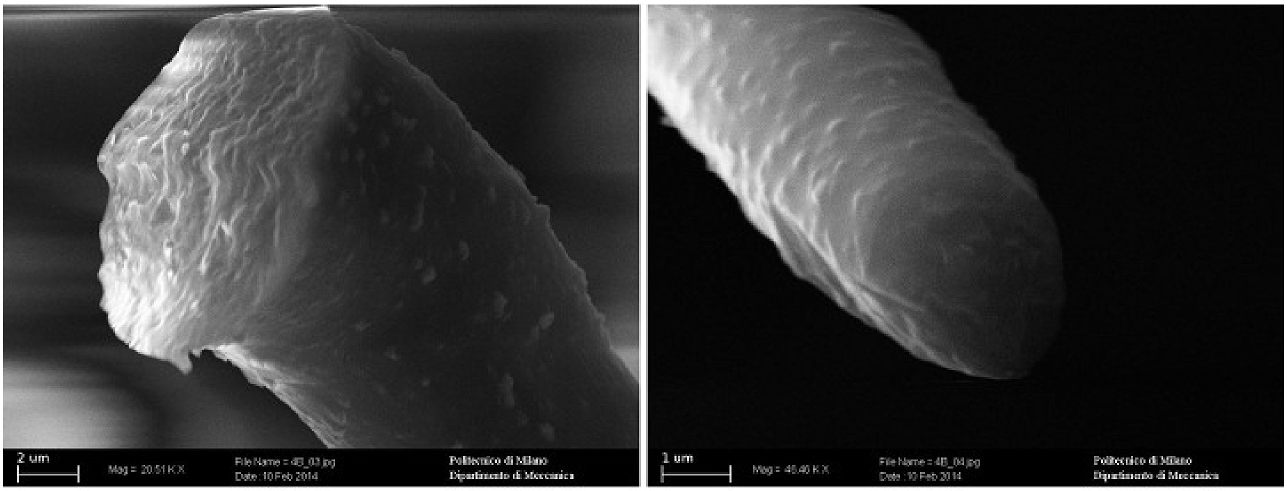


(a) (b)

Fig 9: SEM pictures of the fibers-slag interface at different magnification: (a) 800x and (b) 3000x.

At high magnification (Fig. 10), the fibers surface pointed out several nodules. According to Gualtieri et al. [12] and Comodi et al. [13], those nodules were probably the nuclei of submicronic crystals of cristobalite and mullite. In depth analysis performed by more accurate instruments is still work in progress to ascertain the nature of such surface features.

Compared with the s-1 structure, the s-2 linings seemed to to be unchanged at first glance (Fig. 8d); however, at high magnification (Fig. 8e), some fibers began to melt. Effectively, the chemical composition of the MW fibers induces a lower melting temperature than that of RCFs. At the temperature of the steelworks processes, the fiber melting is not uncommon, especially for the fibers close to the slag. Also in this case, the EDS analysis detected traces of iron and manganese on the fiber surface (Fig. 8f).



(a) (b)

Fig 10: SEM pictures at high magnification of devitrified RCFs.

XRD analysis performed on unused and used RCF-containing linings indicated clearly a partial devitrification of the ceramic fibers contained in the traditional products (Fig. 11). XRD pattern related to unused material highlighted the typical amorphous halo in the range between 2θ = 20-30°. This halo is certainly associated to the vitreous ceramic fibers featuring the lining. However, the identification of the amorphous halo was made difficult by the presence of the quartz particles that act as binder for the support structure (Fig. 11a).

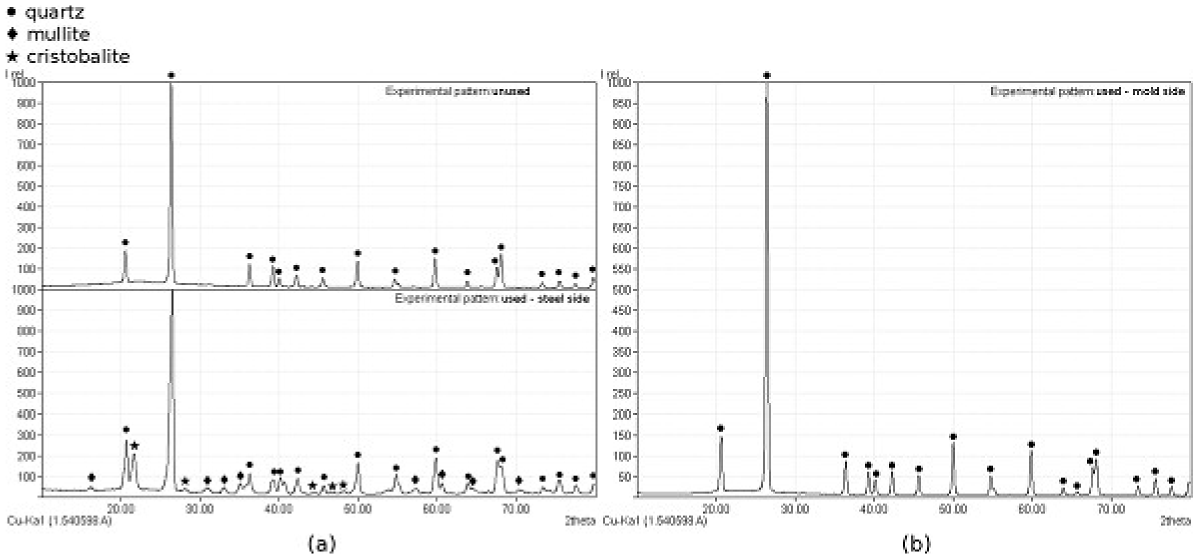


Fig 11: XRD patterns of RCF-containing linings: (a) comparinson between unused and used hot-face material; (b) used cold-face material

After the exposure to the high thermal range, the amorphous halo disappeared and typical peaks associated to mullite and cristobalite were instead recognized in the diffraction pattern of the burnt lining (Fig. 11a). These crystalline products were the same indicated by other researches in the same area [a-f] and represent an unambiguous evidence of the devitrification occurred. Actually, the temperature reached during the ingot castings and the exposure time of the RCFs to this temperature were compatible to those required to completely devitrify the amorphous ceramic fibers [34]. As indicated in the ingot casting simulation performed by Barella et al. [36], during the head feeder filling, the molten steel is characterized by a temperature that implies a solidification time of approximately 4-5 hours (for the ingot size analyzed in this work). Moreover, the ingots are usually stripped after 12-20 hours from the casting operations end. Thus, the linings hot-face is exposed to environmental conditions that stimulate a fast structure evolution, i.e. devitrification.
However, the material behavior was recognized to be different between the hot-face (directly exposed to the molten steel and slag) and the cold-face (in contact with the fold). Actually, the material exposed to the cold-face resulted completely unaltered after the casting operations, as visible in Fig. 11b.

2.2 Case 2: steel foundry castings

As well as the linings employed in steel ingot casting, the sleeves adopted during the foundry tests had the same morphological differences. The f-1 sleeve is featured by a fiber-supported structure associated with subordinated particles (Fig. 12a-b). All the analyzed fibers showed a chemical composition compatible with that of RCFs (Fig. 12c). On the contrary, the f-2 sleeves had a particle supported structure associated to subordinated fibers (Fig. 12a-b). All the detected fibers had a chemical composition that can be attributed to mineral wools (Fig. 12f). The f-2 products were effectively free from refractory ceramic fibers. The main differences between the linings employed in the ingot castings and those used in foundry operations is the dual nature exothermic/insulating of the latter ones. In particular the foundry linings are characterized by the presence of thermogenic elements, i.e. aluminum, that oxidize during the castings operations, heating the molten alloy. This aspect is extremely important to assure a complete filling of the mold preventing the formation of shrinkage cavities and other metallurgical defects.

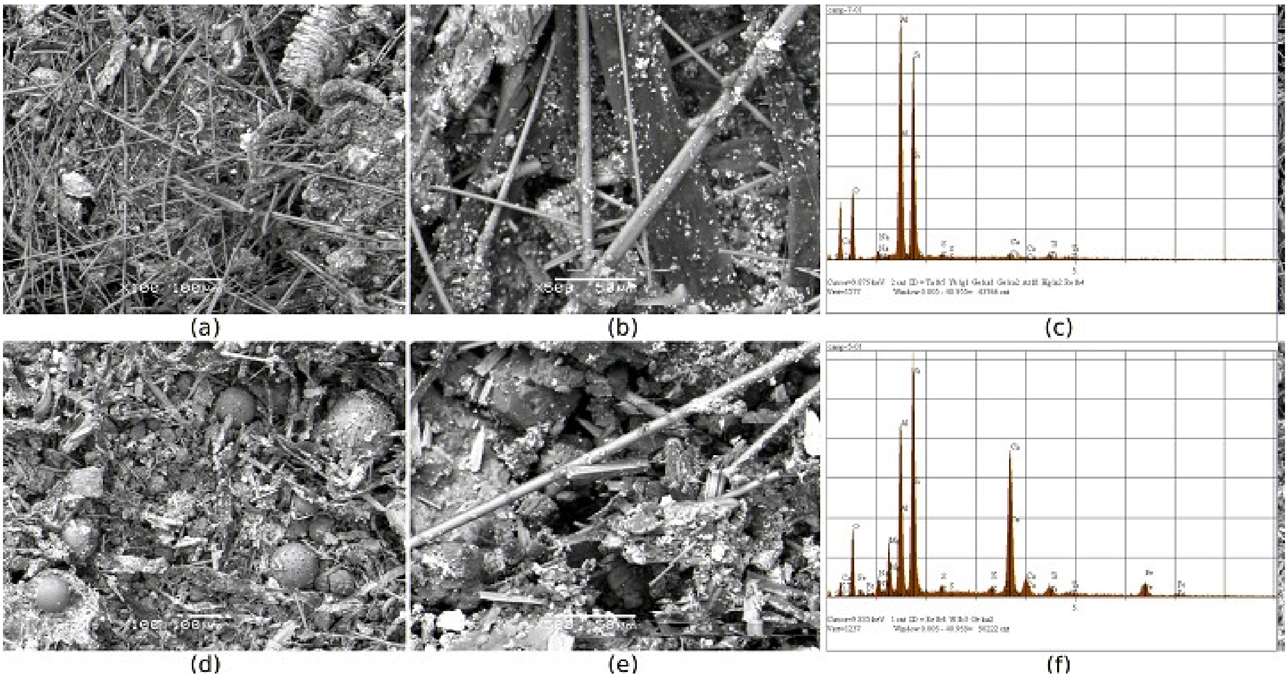
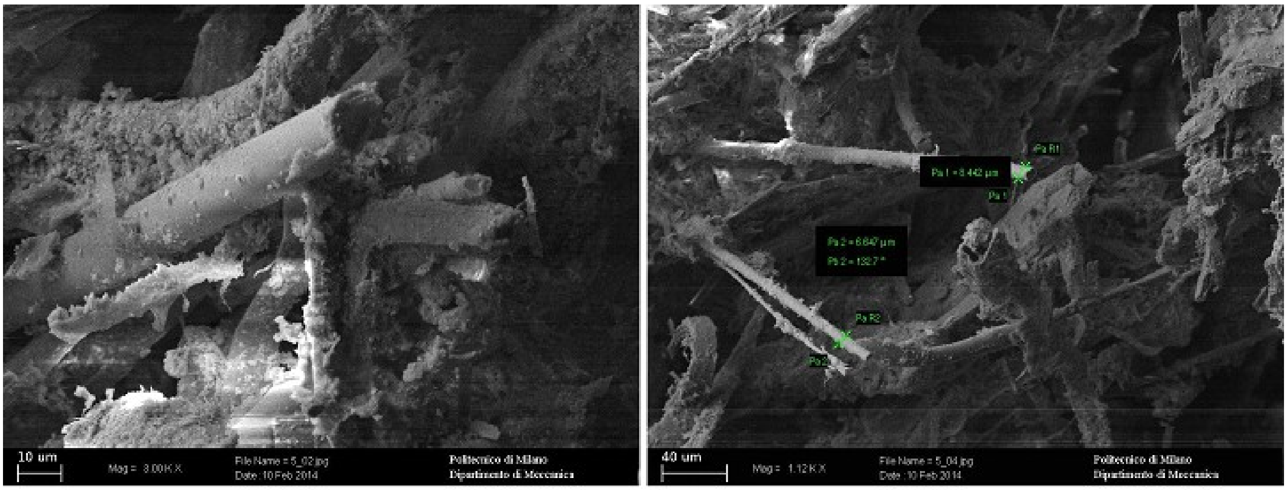


Fig 12: SEM micrographies and EDS spectrum of (a-c) RCF-containing refractory and (d-f) RCF-free refractory.

As soon as the fibers contained in the f-2 products were of the same nature of those used in the s-2 linings, their average diameter weighed on the fiber length was again higher than the limit imposed by the European Regulation (Fig. 13). Thus, the foundry linings can be classified as before as non-carcinogenic because of they completely fulfill the R and Q note of EC 1272/2008.

The obtained mechanical components appeared substantially equivalent from a mere visual point of view (Fig. 14). No appreciable differences were detected on the casting surfaces and on the riser necks. The casting quality was checked through visual tests: both the cast components were free from visible surface defects. In depth non-destructive control was performed exploiting liquid penetrant test that confirmed the integrity of both casting products.



(a) (b)

Fig 13: Detailed SEM pictures of mineral wool fibers charaterizing the f-2 products.

(a) (b)

Fig 14: Pictures of investigated foundry castings: (a) endowed with RCF-containing linings and (b) endowed with RCF-free linings.

The morphology of f-1 products was changed by the use. The most of the fibers appeared broken and covered by the residual products of thermogenic particles oxidation. i.e. aluminum oxide (Fig. 15a-b). For this reason, EDS spectrum showed an intense peak associated to Al (Fig. 15c). Also in this case, traces of Mn and Fe were detected on the burnt fibers. A detail of the small Al_2O_3 crystals deposited on the fibers surfaces was captured in Fig. 16b. In the same pictures big nodules on the fiber surface were detected. In the burnt f-2 products the structure was characterized by the same Al_2O_3 particles detected in the f-1 linings (Fig. 15d). In some areas the mineral wool fibers appeared unaltered without particular morphological and chemical changes (Fig. 15e) whereas in the areas closest to the molten steel, the fibers completely melt (Fig. 16a). In these zone the melted fibers were mixed with the molten steel infiltrated in the lining structure, as confirmed by the peaks associated to Fe and Mn (Fig. 15f).

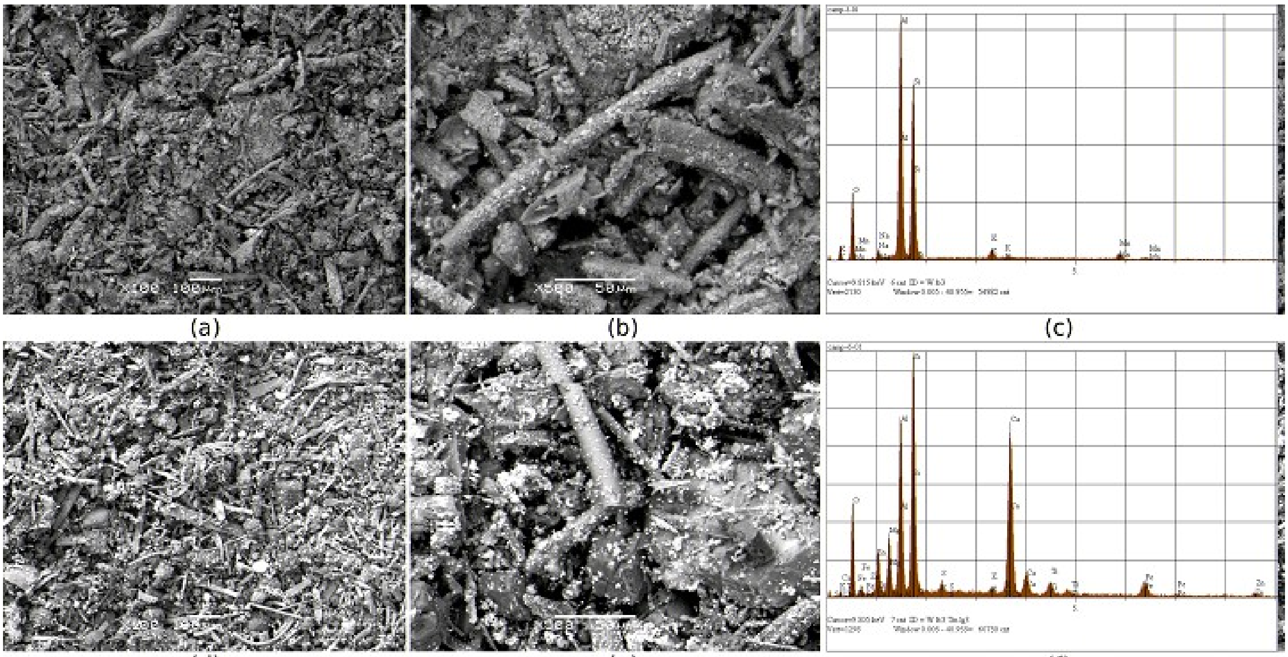
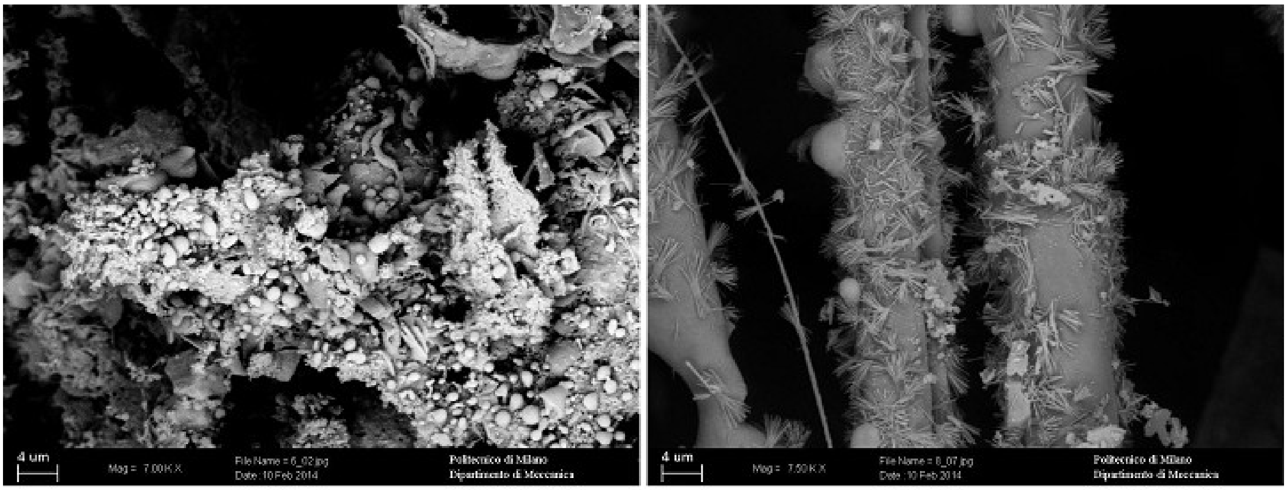


Fig 15: SEM micrographies and EDS spectrum of (a-c) burnt RCF-containing refractory and (d-f) burnt RCF-free refractory.



(a) (b)

Fig 16: SEM pictures at high magnification of (a) melted mineral wool fibers in the hot-face and (b) ceramic refractory fibers covered by Al2O3 crystals.

XRD analysis performed on both unused and used foundry linings better highlighted the changes occurred in the products structure (Fig. 17). Unused products were characterized by a huge amorphous halo associated to the RCFs; intense peaks were instead associated to the thermogenic particles (Al-Si alloy) and to the other particles interesting the support structure (quartz particles). After the service, the diffraction pattern significantly changed. Intense peaks associated to corundum confirmed the thermogenic reaction occurred. Moreover, significant crystallization was pointed out: on the amorphous halo, huge peaks referred to quartz and cristobalite were identified as well as clear peaks associated to mullite were detected. The above mentioned phases are again the same that characterize the devitrification process thus the devitrification is expected.

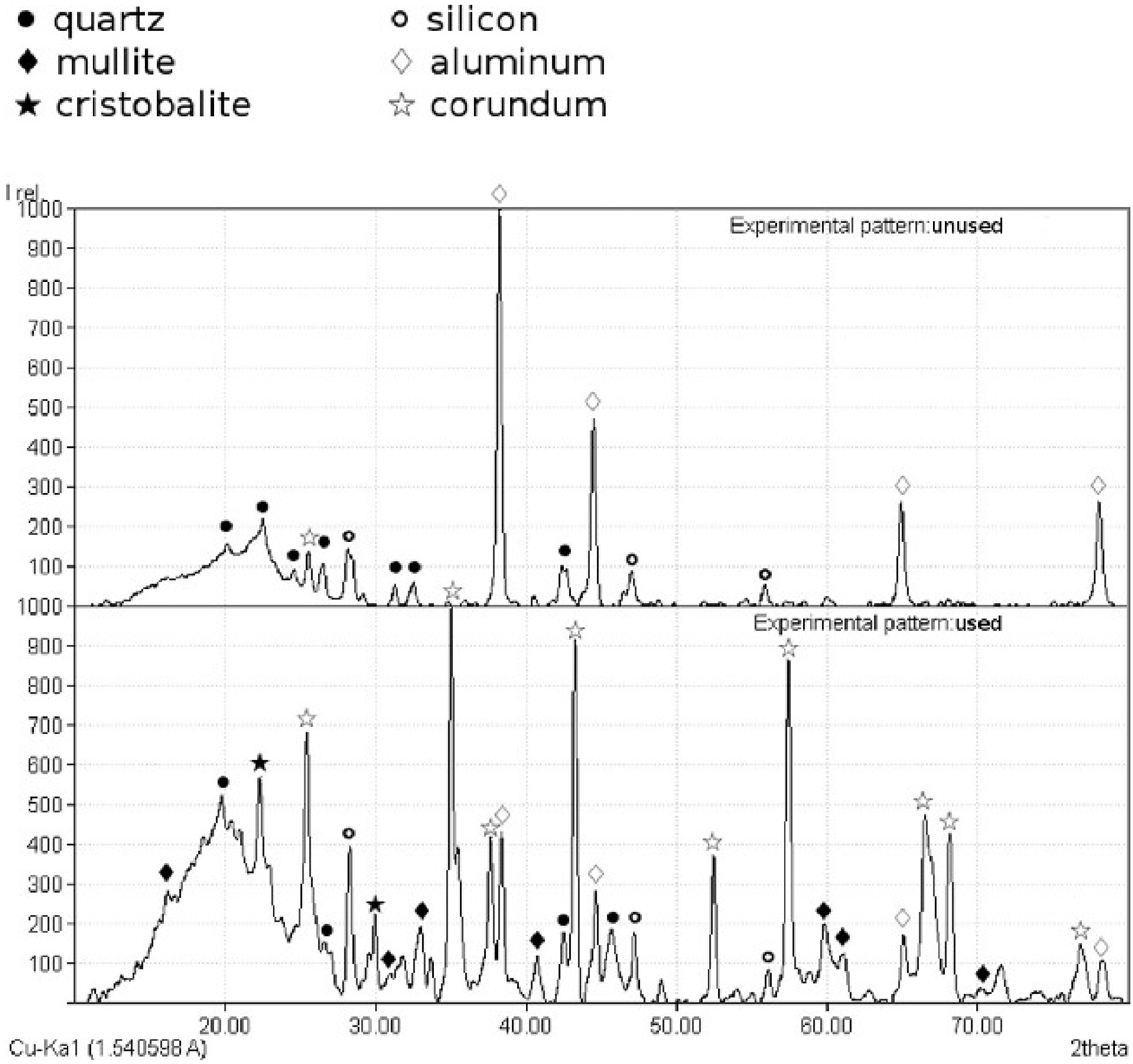


Fig 17: XRD pattern comparison between unused and used RCF-containing linings in foundry castings.

3 DISCUSSION

The obtained results for both the experimental campaigns lead to stress a first conclusion about the RCFs behavior when applied in steelworks applications: the high temperatures featuring the steelmaking processes (ingot or foundry castings) are enough to induce devitrification in the vitreous ceramic fibers, thus leading the formation of crystalline silica, that is classified as carcinogen. In addiction, since the fibrous structures remains practically unaltered enough far from the hot-face, the residual RCFs-containing linings must be still considered hazardous for health and thus must be dismissed by proper way. Moreover, during the ingot stripping, high dust volume is released, freeing in the plants large amount of respirable by-products, causing possible serious consequences to the workers health.
The in-situ tests performed replacing the traditional RCF-containing products with innovative RCF-free products gave important results about the efficacy of the new formulation in terms of metallurgical quality. RCF-free products demonstrated to be technically equivalent to the traditional one, despite of the absence of RCFs in the composition. The tests demonstrated the possibility to save a consistent amount of steel per cast in force of the better insulating capacity of the RCF-free linings. The monitoring of the temperature profiles into the linings during the castings through thermocouples should represent a valid method to demonstrate the better insulating behavior of the new products, and this can provide interesting information about the devitrification process.

Moreover, the RCF-free employment could further reduce the environmental impact of steelmaking operations, lowering the risk to contract lung disease. Further investigation to assess the quantities and the size of the vitreous fibers and of the crystalline phases (in the after service products) must be performed to estimate their degree of breathability.

The in-situ tests carried out in this work open a new scenario about the research of technically equivalent alternatives for RCF-containing applications: the obtained results demonstrated a satisfactory insulation is not granted only by fiber-supported refractories. The innovative products tested in this researches pointed out equivalent or even better insulating properties than RCF-containing products even if constituted by particle-supported structure.

4 CONCLUSIONS

In the present study the changes occurring within RCF-containing side wall linings for ingot casting used in steel plant and within RCF-containing sleeves for risers used in steel foundry were investigated. The achieved results lead to stress the following conclusions:

- the technical equivalence between RCF-containing and RCF-free products for ingot-head lining was demonstrated through direct comparison between the behavior pointed out during the casting of two steel ingots. Both the ingots resulted free from defects and featured by the same metallurgical characteristics;

JODOVIT S.r.l. - Chemical Group
Via Lombardia, 9 – 21015 Lonate Pozzolo
VARESE – Italia
Tel: +39 0331301086
mail@jodovit.com – www.jodovit.com

- the technical equivalence between RCF-containing and RCF-free foundry sleeve was demonstated by direct comparison of two stainless steelfoundry castings. Both the castings resulted free from defects and were characterized by the same metallurgical characteristics;
- RCF-containing burned products showed partial devitrification in the areas closest to the hot-face (directly exposed to the molten steel). SEM observations and XRD analysis allowed to point out the morphological and crystallographic modification of the fibers;
- in both RCF-containing products the expoure time and the process temperature lead to the formation of mullite and cristobalite, typical by-products induced by RCFs' devitrification;
- RCF-containing products conserved after-service significant fibers fraction although became very brittle. The brittleness induced high dustiness leading the dispersion of dangerous particles into the workplace;
- RCF-free products represented a viable alternative to traditional RCF-containing refractories, reducing the environmental impact of steelmaking operations during ingots and foundry castings.

ACKNOWLEGDMENT

The authors would like to acknowledge Mr. Roberto Rizza and Mr. Denis Taboni (Metalcam S.p.A., Breno (BS), Italy); Eng. Marco Fusar Poli (Fondinox S.p.A., Segnano (CR), Italy) and Mr. Fabio Banfi (Jodovit S.r.l.) for the in situ tests and the contributions to the realization of this work. Special thanks to Mr. Italo Campostrini (INGV, Milano) for him strategical help.

REFERENCES

1) L.A. PLUTSHACK, A.L. SUSCHIL; ASM Metal Handbook, Casting, 15, (1992), p. 1273-1278.
2) R.KEITH MOBLEY, Plant Engineer's Handbook (2001), p. 143-147.
3) E.R. NIELSEN, M.AUGUSTESEN, K. STÅHL, Materials Science Forum, 558-559, (2007), p. 1255.
4) WHO (World Health Organization), IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Man Man-Made Vitreous Fibers, 81, (2002), p. 333.
5) T.P. BROWN, P.T.C. HARRISON, Regulatory Toxicology and Pharmacology, 68, (2014), p. 152.
6) ACGIH (American Conference of Governmental Industrial Hygienists), Synthetic Vitreous Fibers (2001).
7) EC REGULATION 1272 OF THE EUROPEAN PARLIAMENT on classification, labelling and packaging (CLP) of substances and mixtures (2008).
8) J.VENTURA, D.M. WOOD; 70th Conference on Glass Problems: Ceramic Engineering and Science Proceedings, Wiley (2019), p. 175-177.
9) N. P. BANSAL, Handbook of Ceramic Composites. Kluwer Academic Publisher (2005), p. 5.
10) A.K. BHATTACHARYYA, B.N. CHOUDHURY, P. CHINTAIAH, P. DAS, Ceramics International, 28, (2002), p.711.
11) M. SCHWARTZ, Encyclopedia of Material, Parts and Finishes 2nd ed. CRC Press (2002), p. 118-119.
12) A.F. GUALTIERI, E. FORESTI, I.G. LESCI, N. ROVERI, M. LASSINANTTI GUALTIERI, M. DONDI, M. ZAPPAROLI, J. Hazard. Mater., 162, (2009), p. 1494.
13) P. COMODI, F. CERA, G.D. GATTA, N. ROTIROTI, P. GAROFANI, Ann. occup. Hyg., 54-8, (2010), p. 893.
14) D.J. DYSON, M.A. BUTLER, R.J. HUGHES, R. FISHER, G.W. HICKS, Ann. occup. Hyg., 41-5, (1997), p. 561.
15) R.C. BROWN, E.A. SARA, J.A. HOSKINS, C.E. EVANS, J. YOUNG, J.J. LASKOWSKI, R. ACHESON, S.D. FORDER, A.P. ROOD, Ann. occup. Hyg., 36-2, (1992), p. 115.
16) L.D. MAXIM, D. VENTURIN, J.N. ALLSHOUSE, Regulatory Toxicology and Pharmacology, 29, (1999) , p. 44.
17) M. LINNAINMAA, J. KANGAS, M. MAKINEN, S. METSARINNE, A. TOSSAVAINEN, J. SANTTI, M. VETELI, H. SAVOLAINEN, P. KALLIOKOSKI, Ann. occup. Hyg., 51-6, (2007), p. 509.
18) T-S. SHIH, P-Y. LU, C-H. CHEN, J-C. SOO, C-L. TSAI, P-J. TSAI, J. Hazard. Mater., 154, (2008), p. 469.
19) EPA (Environmental Protection Agency) – Refractory Ceramic Fibers, II.A.1. Weight-of-Evidence Characterization (1993).
20) U.S. Department of Health and Human Services Public Health Service - National Toxicology Program - 12th Annual Report on Carcinogens (2011).
21) DIRECTIVE 97/69 EC, [23rd update of the Directive 67/548 EEC of 1967, “DSD”, Dangerous Substances Directive, R.C.F. and mineral wools] (1997).
22) WHO (World Health Organization), Workshop on Mechanisms of Fibre Carcinogenesis and Assessment of Chrysotile Asbestos Substitutes (2005).

JODOVIT S.r.l. - Chemical Group
Via Lombardia, 9 – 21015 Lonate Pozzolo
VARESE – Italia
Tel: +39 0331301086
mail@jodovit.com – www.jodovit.com

23) EC REGULATION 1907 OF THE EUROPEAN PARLIAMENT concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) (2006).
24) B.G. MILLER, A. SEARL, J.M.G. DAVIS, K. DONALDSON, R.T. CULLEN, R.E. BOLTON, D. BUCHANAN, C.A. SOUTAR, Ann. occup. Hyg., 43-3, (1999), p. 155.
25) K. LUOTO, M. HOLOPAINEN, M. SARATAHOF, K. SAVOLAINEN, Ann. occup. Hyg., 41-1, (1997), p. 37.
26) A. SEARL, D. BUCHANAN, R.T. CULLEN, A.D. JONES, B.G. MILLER, C.A. SOUTAR , Ann. occup. Hyg., 43-3, (1999), p. 143.
27) M. TOMATIS, I. FENOGLIO, Z. ELIAS, O. POIROT, B. FUBINI, Ann. occup. Hyg., 46-S1, (2002), p. 176.
28) G. VINE, J. YOUNG, I.W. NOWELL, Ann. occup. Hyg., 28-3, (1984), p. 356.
29) B.A. GANTNER, Am. Ind. Hyg. Assoc. J., 47-9, (1986), p. 530.
30) S. KARLSSON, R. LUNDBERG, R. CARLSSON, Journal de Physique (Paris), Suppl. 2, (1986) p. 587, Colloque C1.
31) D. HOLROYD, M.S. REA, J. YOUNG, G. BRIGGS, Ann. occup. Hyg. 32-2, (1988), p. 171.
32) A. ZHEN, S. SONG, Refractories 39-4/5, (1990), p. 19.
33) M. SOPICKA-LIZER, S. PAWŁOWSKI, Thermochim. Acta, 38-3, (1980), p. 293.
34) J.J. LASKOWSKI, J. YOUNG, R. GRAY, R. ACHESON, S.D. FORDER, Anal. Chim. Acta 286-1, (1994), p. 9.
35) M.A. BUTLER, D.J. DYSON, J. Appl. Crystallogr., 30, (1997), p. 467.
36) S. BARELLA, C. DI CECCA, A. GRUTTADAURIA, C. MAPELLI, D. MOMBELLI, Proc. 2Nd Ingost Casting Rolling Forging Conf., Milano (2014).