Insights on characterization of refractory material properties after usage for recyclability determination CESAREF project

Andrea Salerno[a,b,*], Nicolas Tessier-Doyen[b], Elsa Thune[b], Johan Richaud[a], Lionel Rebouillat[c], Severine Romero Baivier[a], Marc Huger[b]

[a] *Vesuvius group plc, Department Refractories Research, 17, Rue de Douvrain, B-7011 Ghlin, Belgium*
[b] *University of Limoges, IRCER, UMR CNRS 7315, 12 rue Atlantis, Limoges 87068, France*
[c] *Pyrotek Inc, Mineral Processing, Iron & Steel Department, 2400 Bd Lemire, Drummondville, QC J2B 6X9, Canada*

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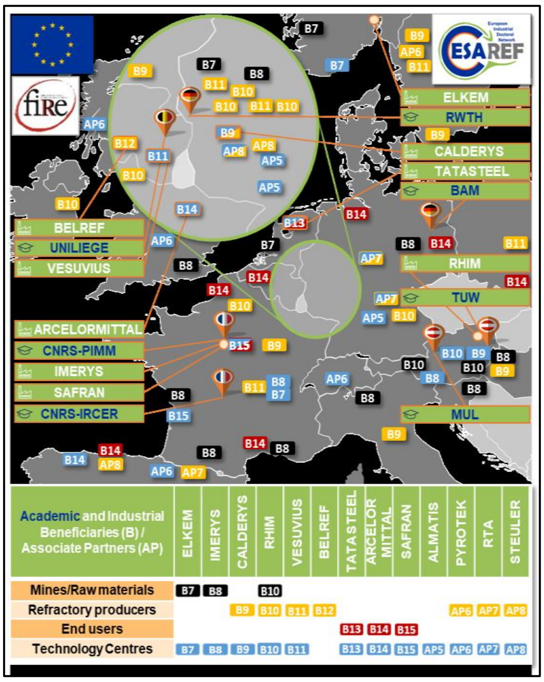
ABSTRACT

CESAREF (Concerted European action on Sustainable Applications of REFractories) is a consortium gathering several European academic and non-academic realities involved in refractory materials research (figure 1, left). CESAREF is supported by the FIRE (Federation for International Refractory Research and Education) international education programs and thanks to Horizon Europe fundings, in particular Marie Skłodowska-Curie Actions, it started his research activities in late 2022. CESAREF is constituted by seven universities and fourteen industrial partners. Its rationale is to train on multi-engineering areas the involved fifteen doctorates to create scientific breakthroughs in the field of refractories for challenges related to the European Green Deal; and also, to strengthen the interconnection within the refractory materials research community.
CESAREF's scientific objectives can be divided in four thematic areas, each one combining empirical, numerical, and environmental topics (figure 1, right). The first area deals with the efficient use of mineral resources and recycling facing circular economy's core challenges. The second area refers to the microstructural design and characterization of refractory materials to increase their sustainability. The third area deals with the fundamental aspects, know-hows, and possible issues related to the future hydrogen-based steel making process. Finally, the fourth area focuses on innovative digital methods and machine learning approaches to improve energy efficiency of steel making process through optimized refractories application and to improve the durability of such materials.
CESAREF consortium guarantees, with the support of FIRE, transversal trainings, international networking, state



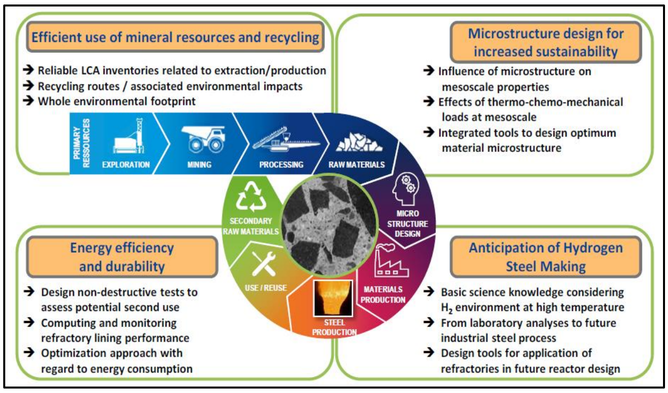


Figure 1: (left) CESAREF consortium including partner organizations from public and private sectors; (right) Thematic areas with respective proposed methodologies and approaches for CESAREF projects.

of the art research activities, and the gathering of prominent figures from refractory materials world coming from academic and industrial positions.

Inserted in the CESAREF context the study briefly discussed here is dedicated to "Characterization of refractory material properties after usage for recyclability determination". The aim of this doctoral study is to provide an insight on the dependence of specific materials' properties (such as thermal conductivity, thermal expansion, Young's module, fracture energy and others) during operative conditions. By mesoscale properties' quantification after one or more using cycles is possible first, to make comparisons with pre-use properties and consequently, to define appropriate Finite Element Models (FEM) to foreseen operative and post-operative conditions of the refractory materials. Thanks to numerical and empirical characterization coupling, is thus finally possible to determine the potential recyclability of refractories.

In addition, the combination of this study with the others belonging to CESAREF project (studies dealing with evaluation of secondary raw materials characteristics, thermodynamic evolutions during operative conditions, life cycle assessment profiles development, improved microstructural design and characterization of novel refractories, machine learning, optimization models and non-destructive testing techniques) aim to create new refractory solutions for steel making industry (and transferrable to other sectors like metal, cement and glass industry) from the micro- to the macro scale fulfilling the full supply chain.

As Bill McCracken said "There would be no life, as we intend today, without refractories. And, without raw materials there would be no refractories. We tend to neglect the importance of sources of raw materials, we take them granted. Our efforts are aimed at the end product neglecting the raw material. We need to get closer to the source." Indeed, there have always been an intricate connection between society evolution and raw materials. The common partitioning of prehistoric periods occurs through the raw materials that enabled progress: stone, bronze, and iron ages. Although advances in materials and technologies have aided development and welfare distribution, unfettered consumption and overexploitation of resources remains a driver for conflicts, geopolitical tensions, and environmental damage. Thus, differently from never before we are looking for technological solutions to ensure progress and at the same time make our way of life more sustainable decoupling economic growth from resources exploitation.

The extraction of raw materials to create solid domestic supply chains in the European Union depends significantly on mid- and long-term investments, and also on appropriate mineral policies. Although the great potential, in terms of mineral reserves, Europe started few new mining activities in the last years.[1] In addition, newly environmental constraints are pushing primary raw materials producers to focus on more profitable and strategic areas such as the one of reuse and recycling.[2–4] These latter indeed, conversely from the trend above mentioned is strongly stimulated by institutional entities and still a small percentage of resources is reprocessed after one lifetime, hence great funds, big rooms for improvements and great opportunities are on that way. Circular economy growth is one of the strategic targets of EU's Green Deal for ensuring raw materials' solid supply chains. Indeed, when end of life materials' collection and treatment is well managed, recycling and reuse practices can ensure great inputs in materials supply. Circular economy advantages concern sustainability improvements by the potential reduction of greenhouse gasses related to extraction and processing of primary resources.[1] Circularity enables a virtuous circle establishing by preserve materials value cutting wastes to the

Table 1 : Concentration of non-novel raw material in function of the number of lifecycles added in the formulation of refractory castable.[8]

Working cycle	1	2	3	4	5	10	20
Primary raw material	100	80	80	80	80	80	80
Secondary		20	16	16	16	16	16
Tertiary			4	3.2	3.2	3.2	3.2
Quaternary				0.8	0.6	0.64	0.64
Quinary					0.2	0.128	0.128
Senary						0.03	0.03
Septenary						0.005	0.005
Octonary						1.00E-03	1.00E-03
Nonary						2.00E-04	2.00E-04
Denary							5.00E-06

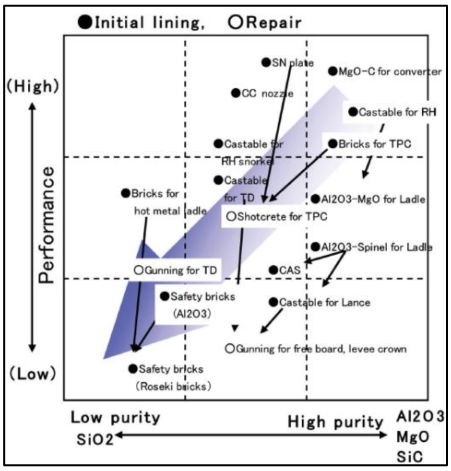


Figure 2: Possible application of refractories depending on purity and performances in the frame of downscaling closed-loop recycling strategy.[8]

minimum leading to emissions reduction and boosting profitability in combination and thanks to reliable sources of materials hence inducing synergies within transversal industrial sectors and attracting investments.

Refractory materials are, for definition, supposed to resist to high temperatures (above 600 °C) and also to chemically aggressive conditions. Furthermore, they need to withstand various mechanical stresses. Thus, physical, chemical and thermodynamic stability are key parameters for refractory materials design. Refractories are mostly used in basic metal industries where they act as confinement for the molten metals by ensuring safety and costs during the production process. They insulate steel vessels and supports from overheating and destruction. Secondarily, the refractories enable heat loss control so the energy costs of the process. As a consequence, refractory materials and the systems of them need to overcome thermal, chemical and physical stresses like shocks, long time exposure, impact loads, and many others.[5]

Worldwide refractory production is reported to be near 40 million tons per year with strong fluctuations determined by the iron and steel industry which is responsible for more than the half of the total demand.[6] During the operational period in a steel-making industry nearly 40% of the total refractories are consumed and replaced every year.[1,7] Some virtuous cases in reduction of refractories consumption are isolated, in Germany and Japan, for example, has been registered refractories consumption per ton of steel at the lowest in all world: roughly 7 kg of refractories per ton of steel produced.[3,8] Nevertheless, the worldwide average value reported is attested slightly above 10 kg per ton of steel.[9] Thus, considering the crude steel production in 2021 reported by the World Steel Organization, 1’951 million tons,[10] the amount of spent refractories worldwide only associated to steel production corresponds to approximately 20’000 tons per year. Considering these numbers and the tendency discussed above, recycling is going to catch on more and more over the years.

However, is important to distinguish between recycling practices to be able to maximize the intrinsic value and potentiality of the waste. Indeed, two ways of recycling are generally distinguished: closed-loop and open-loop recycling. [11] In the former case, the properties of the waste are considered not far from the ones of the primary raw materials. Hence, is possible to reprocess the materials and reintroduce them in the same circle of production (this is what occurs in the steel recycling process for example). In the latter case, the operative conditions lead the material to change its properties resulting in differences with respect the primary raw materials. In this frame, the wastes are considered suitable for other applications substituting other materials (this is the case of near all the refractories recycling practices put into operation nowadays, consisting in using spent refractories to produce roadbeds or other applications with low economical value). Is evident that the closed loop recycling has the potential to keep the value and functionality of end-use materials as constant as possible. Furthermore, closed loop recycling contribute in a significant way to the development of circular economy.

Beside these practices based on waste hierarchy and value-based concept, a functionality and purity classification has been reported by Hanagiri et al. in the late 2008.[8] The concept of purity of a refractory material and related performance are strictly correlated; thus, considering Nippon Steel strategies this research project aim to find similar solutions in the case of steel flow isostatically pressed materials (Al_2O_3/C and ZrO_2/C) and insulating boards (Vermiculite). A first strategy consists in the addition of the nth raw materials in the novel formulation and depending on the number of lifecycles to which the waste-derived raw materials have been subjected the quantity varies. Indeed, to keep high performances in the materials have been reported by several authors the critic threshold of 20% of non-novel raw materials in the formulation.[11–14] Thus, by increasing the number of life cycles the respective derived raw materials added to the new formulation is decreasing drastically. In table 1 is reported the case of the castable formulation production with recycled raw materials in an amount dependent on their lifecycle.[8] A second strategy is based on the downscaling of the raw materials (figure 2), overcoming the needs for constant high purity and high performances. Essentially, by increasing the impurities (proportional to the number of life cycles) there occur the application in refractories less performant hence with lower purity needs. These solutions combined together can be some of the good practices to repress open-loop recycling generating strong incentives and interests in the closed-loop circularity of refractories.

Additionally, is worth to distinguish between the additional phases and components (the so-called impurities) present in the end-of-life refractories with respect to the refractories constituted only by primary raw materials. [11] Chemicals like calcia, iron oxides, silica can have an impact on the refractory performances due to in-use low melting phases formation, high volume variations, incompatibility with slag or molten metal, high porosity development, and others resulting in materials’ service lifetime reduction and interfering with the steel quality. Nevertheless, other components such as high thermal and corrosion resistant chemicals and phases developed during operative lifetime like spinel or structural reinforces such as nano whiskers can increase durability and performance of the refractory materials. Indeed, thermodynamic considerations based on Gibbs free energy minimization of the system refractory-molten metal-slag in particular conditions have to be taken in account.

The main issue for the correct exploitation of such interesting characteristics derives from two main problems. The first is about the lack in thermodynamic simulation of the system evolution during the in-use conditions. Appropriate computational software like FactSage® has been developed in the past years and are continuously taken more and more space in the field of refractories. The second problem, pertinent to this study, regards the fact that mechanical behavior of most of the refractory materials is complex and difficult to determine because of their nonlinear behavior derived from the heterogeneous nature and the multi-phase composition. Reliable investigations on the meso- and macroscale of the refractories system require the use of computational methods, such as finite element analysis (FEA) to further obtain accurate thermal and mechanical materials' properties evolution and behavior during operative conditions.[15,16] The need for the numerical tools derives primarily from the nonlinear thermomechanical character of the materials, but also from the strong complexity of the refractory systems and the great variety of interactions among the molten metal, the impurities contained in this latter, the process parameters, and many other factors.[17,18]

The literature review indicates a need for quantifying thermal degradation of the refractories during operative conditions.[17,19–22] To do this, in the frame of numerical analysis, an experimentally validated thermomechanical model will be developed with ABAQUS® software to evaluate and predict refractories' properties variation (Young's module, modulus of rupture, thermal dilatation, thermal conductivity, and others) during the thermal cycling typical of pyrometallurgical and other high temperature processes. During this study mesoscale modelling will be taken in account due to computational expenses, complicate analysis and details needed to develop a thermomechanical model for a system of refractories (such as an entire lining for example), and due to nature of the materials studied (isostatic alumina- carbon and zirconia-carbon refractories do not belong to linings or other systems but to precise products, such as slide gates and shrouds). The results obtained from the mathematical model will be further compared with empirical results obtained at different temperatures from thermal dilatation measurements, crush, brazilian, triaxial test, and high temperature evaluation of Young's modulus and modulus of rupture.

Furthermore, the aim of this thesis will be the development of a methodology and so a strategy to predict the recyclability which can be applied, after the application of proper expedients, to the recycling potential prediction of various refractory materials. To obtain this, thermomechanical model to have insights about end of life materials' properties, compositional models to foreseen phases and chemicals in the spent refractories, and multi criteria decision approaches based on machine learning to achieve sustainable and profitability goals are needed to work in combination.

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