INSIGHTS ON NUMERICAL MODELS TO PREDICT POTENTIAL RECYCLABILITY OF SPENT REFRACTORIES FROM STEEL MAKING INDUSTRY

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ABSTRACT

The present study is part of the CESAREF (Concerted European action on Sustainable Applications of REFractories) doctoral network started in late 2022. The aim of the consortium is the contribution to scientific breakthroughs inherent to refractories for steel making sector thanks to transversal competences deriving from academic and industrial realities. European green deal and circular economy targets set by EU for 2025 are also related to the massive consumption of refractory materials in the steel industry. Operative lifetimes of refractories range from hours to several months depending on their role. As a result of increasingly tightened policies and disposal costs, and due to recent supply chain shortages, end-of-life refractories recovery and recycling practices are receiving great attention. Some of the core requirements for sustainability and circularity are the reduction of open-loop and down scaling strategies, to maintain refractory materials value as long as possible, of the end-of-life materials. Over the years application of numerical models has proved to be a useful strategy for researchers facing in-use issues related to refractory materials. In this study, different finite element models (FEM) applied to end-use refractories are discussed to understand their suitability for potential recyclability prediction. Thermomechanical characterization of prior- and post-use materials allow to identify the critical issues related to numerical models' development. The comparison between empirical results and the appropriate numerical model allow us to identify suitable pathways to improve refractories sustainability.

CONTEXT

There has always been an intricate connection between society's evolution and raw materials. In fact, 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, we are looking for technological solutions to ensure progress, and at the same time make our way of life more sustainable by decoupling economic growth from resources use.

The recent European Union directive regarding wastes introduced a hierarchic strategy to be adopted for waste reduction and circularity improvement.[1] The preference order established by the directive is set as: prevention, re-use, recycle, recovery, disposal. Furthermore, circular economy growth is one of the strategic targets of EU's Green Deal for ensuring raw materials' solid supply chains.[2]

One of the main sectors involved in the green transition is the iron and steel industry, for which ambitious sustainability targets have been set for 2050. Starting from the iron ore to get the final product an energy intensive process is needed. World average data reports CO_2 emissions equal to 2 tons per ton of steel produced.[3] That is why EU is strongly pushing steel producers towards more efficient and lower energetically intensive production processes. Hence, projects such as CESAREF (Concerted European actions on Sustainable applications of REFractories) are put in place receiving great attention from the academic and industrial sectors. CESAREF is a big European consortium of universities and companies acting together with the aim of training different doctorate students on excellent science to create breakthroughs in the field of refractory materials for the steel industry.

INTRODUCTION

Steel embodies a vast class of iron alloys containing carbon in the range between 0.002 and 2.14 wt.%. Steel making occurs through the casting process and nowadays the most used method is the continuous casting, counting for more than the 96% of total steel produced.[3] A modern continuous casting system is composed by three main parts: the ladle, the tundish, and the cooling zone (figure 1). A ladle is a big reservoir of liquid steel (able to contain from tens to several hundred tons of liquid steel) which is then poured into the tundish. The tonnage of the ladle corresponds to one heat, and the number of heats performed with one tundish corresponds to one sequence. The tundish acts as reservoir of molten steel and distributes the liquid metal into the multiple casting molds where steel solidification starts. The tundish stores a small amount of molten steel while dispensing part of this latter elsewhere with general purpose to regulate flow and achieve a steady output with intermittent inputs.

The tundish has the roles of molten steel distribution, buffering, flow control, purification, and heat loss limitation. To nicely exploit the above-mentioned functions many refractory materials are used in the tundish:

- refractories to control and homogenize the liquid metal flow in the vessel (dams, wires, impact pads, purging plugs);
- refractories to enable the steel to move safely with no oxidation limiting material and energy losses from one reservoir to the following, these products can be submerged entry shrouds (SES), submerged entry nozzles (SEN), stoppers, and slide gates;
- refractories to separate and isolate the external steel shell from the molten steel ensuring safety and energy savings, these materials are called lining refractories.

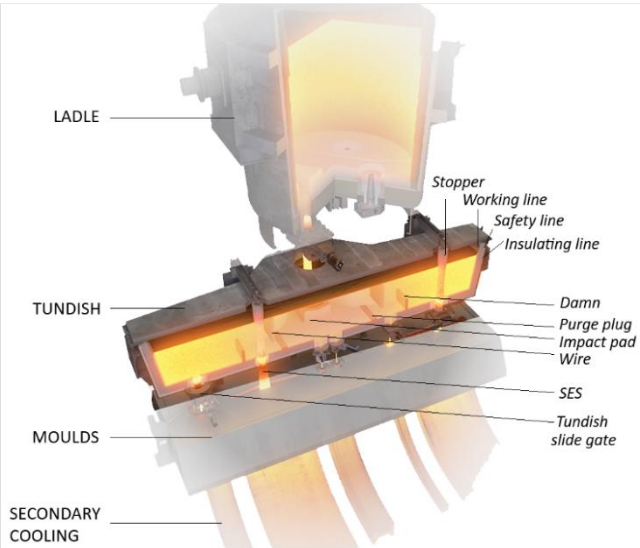

Figure 1: elements in the continuous casting process for steel production and some of the refractory parts used for the tundish. Reproduced with the courtesy of Vesuvius plc.

Commonly the lining refractories can be distinguished depending on their position: the working lining is directly in contact with steel and slag, the permanent lining, in between working and insulating lining, is supposed to compensate stresses and to allow operations safeness in case of working line failure; and insulating lining reduces heat exchange between the previous linings and metallic shell. Some of the above-mentioned refractories are highlighted in figure 1 and various refractory products, grouped by their applications, principal functions, main failure mechanisms, average lifetimes, and some of the possible refractory composition that are commonly used, are provided in table 1.

STRATEGY AND PERSPECTIVES

The thermo-mechanical behavior of most of the refractory materials during operative conditions is complex and difficult to determine and foreseen. The reasons behind are their nonlinear responses to stimuli derived, in part, from heterogeneous nature and harsh operative conditions. Due to that, reliable investigations to improve refractory products lifetime require the combination of experimental analysis and computational methods, such as finite element analysis (FEA).[4,5]

Additionally, to tackle waste production, the re-use and recycling practices need to be fully exploited. In the former case, re-use, the ageing of key thermomechanical properties of the refractories during usage can be assessed and deployed, in combination with the operative conditions severity, into an adapted Failure Modes, Effects, and Criticality Analysis (FMECA). The purpose is to obtain qualitative and quantitative reliable information on the lifetime of the refractory product for a particular application. Furthermore, end-of-life refractories recycling is another key step related to sustainability. During spent material sorting, compositional evaluation, sieving, and other pivotal steps, great bottlenecks must still be overcome. On top of the technical recycling passages, a proper algorithm able to predict profitability has not been developed yet. Hence, this project will focus on the adaptation of a Multi Criteria Decision Approach (MCDA) for refractories sorting based on their intrinsic characteristics, to define recycling convenience.

Experimental characterization and numerical modelling

Refractory materials are, for definition, supposed to resist high temperatures, chemically aggressive conditions, and various mechanical stresses. It is possible to discriminate between stress and strain-controlled loads.[6] The first are the function of the structure's geometry and its density. The latter, strain-controlled loads, can derive from thermal expansions, creep, or structural constraints. They are function of the material's properties, as for example the thermal expansion coefficient, Young's modulus, Poisson's ratio, thermal conduction, porosity, and others.[4] Refractories for steel-making industry are primarily exposed to thermal loads and, as a response, most of them undergo in softening enhancing the plastic behavior at high temperatures. This is the reason why a strong focus will be given in this project to the key thermomechanical properties variation and elastoplastic laws governing the materials behavior. In particular, attention will be paid on the evolution of thermomechanical properties from prior to after usage state. Identification of the pivotal properties and simulation, through the proper yielding function, of the material behavior, are crucial priorities to enhance the performance of the products, hence tackling the prevention step of circularity.

Refractory materials for tundish linings will be at the center of the research. For example, insulating boards composed mostly of vermiculite will be investigated. Previous works, on the carbon pick-up of similar material utilized in the ladle, identified the thermal properties degradation triggering factors. Densification, impurities diffusion, secondary phases formation, and permanent shrinkage are expected phenomena that will be experimentally assessed during this research's post-mortem experimental characterization.[7] These key properties are also related to the operative conditions such as thermal enhanced diffusion, compressive and shear stresses due to lining system's architecture, but also to the cyclical thermal gradients related to continuous charge-discharge steps. Hence, it is possible to consider periodic fatigue cycles and the proper finite element model is needed not only to identify the magnitude and location of the critical loads (thermal and mechanical), but also to further extrapolate their impact on properties degradation.

Over the years, many yield functions have been developed to explain the plastic behavior and consequent failure of various material classes. The Mohr-Coulomb, Tresca, von Mises, and Drucker-Prager are some of the most known criteria describing specific materials' yielding under particular conditions.[8,9] These above-cited yield laws show some critical drawbacks such as the necessity to evaluate shear and tensile yielding stresses to define ranges of applicability, the approximation to homogeneous material's properties, and the non-exhaustive behavior prediction in certain regimes. For these reasons, over the years, several yield criteria have been proposed. In particular, Bigoni D. and Piccolroaz A. developed a modulable criterion for which is possible to modify the yield function.[10] The model is based on a phenomenological based yield criterion (the yield function is directly obtained from interpolation of experimental data) valuable in predicting the mechanical behavior also of ceramic materials

Table 1 : Overview of products, functions, properties, failure mechanisms, lifetime, and some of the compositions for tundish's refractories.[4,6,7,14]

APPLICATION		PRINCIPAL FUNCTIONS	MAIN FAILURE MECHANISMS	LIFETIME	COMMON COMPOSITION
Steady flow control	Dam/wire/multilayer filters	Ensure uniform liquid steel flow and temperature distribution also preventing inclusion flow	Corrosion Erosion Thermal shock	5-20 heats	Alumina-magnesia-carbon Alumina-silica-carbon High purity alumina/magnesia
Steady flow control	Impact pad	Control molten steel from ladle impact and reduce inclusions spread	Corrosion Erosion Thermal shock	5-20 heats	High alumina or magnesia Alumina-magnesia spinel Magnesia-chrome
Flow control	Submerged Entry Nozzle (SEN) Submerged Entry Shroud (SES)	Feed molten steel from tundish to mold, suppress oxidation and nitrogen pickup, reduced heat loss	Corrosion Thermal shock Clogging	10-30 hours	Alumina-silica-carbon (body) Magnesia-carbon (seat SEN) Zirconia-graphite (sleeve SES)
Flow control	Tundish slide gate	Control liquid steel flow rate from tundish to molds	Bore hole erosion Surface abrasion Steel infiltration	5-10 heats	High alumina/magnesia Alumina-magnesia spinel AZC (alumina-zirconia-carbon)
Lining	Working line	Contain molten steel ensuring operations quality and safety	Corrosion Cracks propagation Spalling	5-20 heats	High purity alumina/magnesia Zirconia-carbon (slag line) Magnesia-Chrome
Lining	Insulating line	Reduce the thermal diffusion in steel shell and energy losses	Permanent shrinkage/densification Tensile/compressive failure Working/safety lines failure	20 heats - 1 sequence	Vermiculite Alumina-silica fibers Magnesium-silicate

sensitive to pressure. The flexibility shown by the criterion is appreciated in the field of refractories since, during their processing and working conditions, many changes occur.

Fatigue and Failure Modes, Effects, and Criticality Analysis

Experimental and numerical modeling are not always sufficient for failure prediction and materials' behavior foreseen. Commonly, lifetime evaluation is a complex practice in the field of refractories used in continuous casting process due to their heterogeneous nature, complex geometry, and strong variety of stresses to which they are subjected. Additionally, the possible failure mechanisms associated to a particular product in a specific application are not due to a single parameter. Different failure mechanisms can be observed for the same refractory application. Although in recent years, the research on refractories has made great strides obtaining strongly performant materials, few researchers have applied the fatigue theory to refractory materials. This kind of analysis is widely used in many engineering fields to predict the lifetime of ductile materials such as metals. Examples are the Goodman-Haigh and Gerber diagrams frequently adopted by structural engineers in case of low- and high-cycle fatigue cases. Previous studies on refractory materials have reported several mechanical failure mechanisms under cyclic loadings. The identification of preferential cracks propagation paths, damage saturation, cracks coalescence and interlocking, and grains relocation mechanisms are a result of fatigue inside the material.[11] Furthermore, the turning point has been the link of these individuated energy dissipation mechanisms with the key thermomechanical properties of the material to define the lifetime of the material.[12]

Failure Mode, Effects, and Criticality Analysis, FMECA, is a strategy adopted in the last century to assess the operativity and reliability of a product through inductive reasoning. Essentially, the analysis consists in individuating the ways or modes in which the product could fail, understand the consequences of such failures on the products operativity and on the overall system, and finally define criticality and severity levels for each of the individuated failures and related effects.[13] The adaptation of this approach could enable a more rigorous and statistic treatment of failure analysis allowing the incorporation of fatigue in the investigation. The frame of this strategy is to improve the utilization of a product enhancing the re-use by identifying the proper actions to reduce waste generation. In this context, it is possible to perform both qualitative and quantitative analysis because of the integration of significance measure through criticality analysis. By generally adapting the quantitative evaluation of each i-th failure mode, the related criticality number, C_i, can be defined as:[13]

$$C_i = \alpha_i \beta \lambda_n t \quad (1)$$

It is worth specifying each of the parameters composing the equation. The failure mode ratio α_i can be defined as the probability (expressed in decimal fraction) that the product or a part of it will fail in the i-type mode. It represents the diverse ways a system or a part of it fails. This number is statistically derived and is given as a percentage of the total observed failures. The condition probability, β, of operational failure represents the probability that the identified failure mode will cause the product failure due to the ageing or degradation of the key properties related to the identified i-type failure mode. The component failure rate λ_n represents the number of particular n-parts of the product which are subjected to the i-type failure mechanism. At last, t corresponds to the total operational time the product has been utilized.

Afterwards, a severity classification of the operational conditions is built. To do so, the numerical modeling already performed will assist the purpose. The outputs from Finite Element Analysis are the maps of stresses, strains, pressures, and other parameters. From these, is then possible to quantify operative conditions severity. Comparing the output fields to the experimentally determined key properties of the material prior usage, it is possible to classify the severity in four categories: negligible, marginal, critical, and catastrophic. Finally, the lifetime space (figure 2), including a criticality function proper for the product in the specific application, represents the link between severity conditions and probability of occurrence, or criticality number, for each system's failure modes and parts. Four different levels can be thus defined related to the fatigue and the lifetime of the material: i) unacceptable criticality, the product is considered no more suitable for that specific application, ii) high criticality, the product can be considered in necessity of repair (at the specific n-part) before further use, iii) and iv) moderate or low criticality, the product's resulting properties can be considered appropriate for an additional life cycle, thus tackling re-use target.

Multi criteria approach for refractories recycling

As previously said, during steel production the smelted material passes into several furnaces and vessels. Each of these containers has its own type of refractories used for specific needs. Thus, at first glance, the collection sorting and categorizing step is one of the first bottlenecks for refractories waste recycling. An additional blocking point in refractories recycling consists in the crushing/pulverization of the materials to remove impurities or better homogenize the end-of-life materials. But, besides these steps, it is strictly necessary from an environmental point of view and for energy and resources usage, to identify the convenience of recycling. Thus, it is important also to distinguish recycling practices. Indeed, two ways of recycling exist: closed-loop and open-loop. In closed-loop recycling, the value of the waste is considered not far from primary raw materials' value. Hence, it is possible to reprocess the materials and reintroduce them in the same circle of production. Conversely, in open-loop recycling, the operative conditions lead the material to a dramatic change resulting in lower value with respect to the primary raw materials. This latter case is common for all the refractories recycling practices put into operation currently. In literature, many cases of open-loop recycling can be found. Most of the postmortem refractories are recycled in roadbeds, slag additives or conditioners, aggregates for clinker and for the cement industry, and as soil neutralizers and flowerbeds.[14] It is evident that the closed-loop recycling has the potential to hold end-use materials' value and functionality constant. Furthermore, closed loop recycling contributes in a significant way to the development of

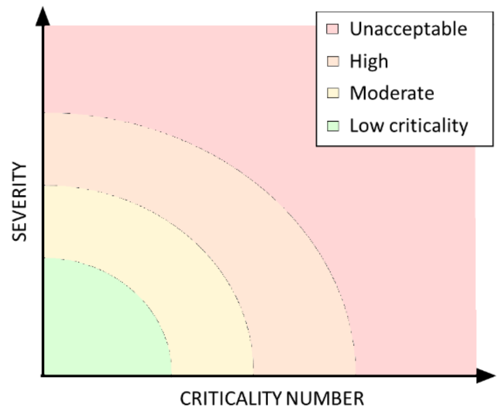

Figure 2: Criticality space representing the criticality number and the severity relation defining refractory product's lifetime.

circular economy. That is why the development of more powerful strategies may help in keeping up the value of the spent material as much as possible. Since there is a wide variety of aspects to consider, a multiple criteria decision analysis could be the key. After processing, refractory materials can have, for example, oxides and/or elemental impurities, steel residues, crystallographic phases developed during the operations, structural instabilities, morphological variations. Thus, it is necessary to assess the additional properties and specifications for the end-of-life material that can have an impact on further applications if inserted in a specific refractory formulation. To distinguish between valuable compositions in terms of purity, economic value, possible resulting thermomechanical properties in a refractory product, or other parameters, an interesting approach may be the adoption of multi criteria decision approach (MCDA). This latter is a strategical method to evaluate the best option or the set of more convenient options in the framework of problems involving many variables. In brief, the multi criteria problem can be mathematically seen as the need of maximization for a global value function, $U_{d_{(g_l)}}$, dependent on a marginal value function of the x-component possessing a certain l attribute, $u_{(d_{(g_l)})}$, and the relative attribute weight, p_l:

$$U_{(u_d)} = \sum_{l=1}^{s} p_l u_{(d)} \tag{2}$$

where $d_{(g_l)}$ corresponds to the evaluation vector of the x-component with l-th attributed in the level g.

With this strategy, a study has been recently performed on the feasibility of the application of a linear multicriteria decision analysis coupled with an on/off criteria to sort spent refractories, also in the frame of sustainable targets. [15] The study proved the good versatility of the method and the possibility of its adaptation to end of life refractories case. Big rooms for improvement are still needed and a proper adaptation to the case of recycling is necessary but a glimpse of feasibility has been observed.

CONCLUSIONS

European Green Deal has set big technological and scientific challenges for steel making sector to achieve sustainability, circularity, and environmental impact requirements for 2050. CESAREF consortium aims to help in creating breakthroughs in the field of refractory materials for steel making transferrable also to other sectors. For this research, focus will be put on the refractory materials for the tundish linings. One of the possible strategies to tackle the European challenges considering as reference key steps, the waste hierarchy can be the identification of the key properties to be assessed depending on the refractory application requirements. The tested properties may be used as inputs in numerical simulations to obtain a clear view of failure and yielding phenomena occurring in refractories. Furthermore, key properties aging, obtained from the comparison of pre- and post-usage refractories, linked with fatigue theory could help refractory producers in more rigorous evaluation of products lifetime. The dependency of properties degradation, operational conditions, and statistical information may be considered for an adapted Failure Modes Effects and Criticality Analysis to obtain reliable qualitative and quantitative investigations of the refractory materials conditions. Moreover, a linear algorithm has been proposed and further tests in that way will be presented soon to optimize it for specific cases. Besides prevention and re-use, to tackle recycling in literature, a large variety of cases have been observed in the frame of open-loop recycling. Hence, big efforts are needed to progress in closed-loop recycling. Many factors must be considered to efficiently solve the recycling reliability problems related to the spent refractory materials. To take forward this bottleneck, a Multi Criteria Decision Analysis (MCDA) has been proposed. This latter approach has recently proved to be efficient for refractories wastes disposal in sustainable framework. Therefore, it opened possibilities for its adaptation in the case of reliable and predictive recyclability determination.

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