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CONTENTS

RECYCLING REFRACTORIES FOR STEELMAKING PROCESSES

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Review paper

ABSTRACT

The objectives and effects of refractory materials recycling, as well as the potential industries from which waste refractories suitable for recycling can be collected, will be discussed in this paper. After the end of its service life, the refractory material is usually disposed at industrial landfills or recycled. The main motive for reuse of refractories is the sustainable conservation of natural resources and the environmental protection by reducing CO_2 emissions and industrial landfills, reducing landfill costs and users' costs. The effects achieved by refractory materials recycling are the cost savings of raw materials and disposal, the improvement of the environment, the product line expansion, and consequently the opportunities for products' placement in hitherto unknown and inaccessible markets, as well as closer cooperation between users and suppliers. Respecting recycling policies brings us closer to the concept of zero waste.

Keywords: *refractories, waste, recycling, steelmaking processes*

1. INTRODUCTION

Refractories are indispensable for all high temperatures processes, such are the processes in the metal, cement, glass and ceramics industries. During these processes refractory materials can be in contact with corrosive liquids or gases, which influences their life time. Control of the refractories requires repair (if possible) or replacement of parts or all refractory lining. If they are not recycled, refractories become waste materials.

Economic aspects of refractories recycling are related to the industry where the usage of refractories is large, such as steelmaking and its processes. For this purpose, different types of refractories are often used, and so in large amounts.

Depending on the requirements of the application, there is a huge variety of refractories. There are different ways in which refractory materials can be classified, with the most common one being based on chemical composition (acid, basic or neutral), type of bonding (tempered, fired) and method of installation (shaped or unshaped) [1]. Based on a recent review (table 1), the most used refractories worldwide are refractory clays (46 %) and magnesia-based refractories (26 %) [1].

Table 1. World refractory raw materials consumption [1]

Raw Material	World consumption, (%)	Primary Source Country
Refractory clays	46	China
Magnesia	26	China
Recycled refractories	7	China
Calcined bauxite	4	China
Brown fused alumina	3	USA
Doloma	3	China
Tabular alumina	2	China
Calcned alumina	2	South Africa
Graphite	1	China
Calcium aluminate cements	1	Australia

When it comes to refractory clays, it can be claimed that they are used in a wide range of applications and industries, while magnesia refractories are proved to be very important for the steel industry. Although with a small (global) distribution of just over 3 %, doloma has strong bonds with the stainless steel industry, and outside of China, doloma based refractories have largely replaced magnesia-chrome bricks. Worldwide refractory production is thought to be around 35 – 40 million tons per year, with annual fluctuations governed mostly by the iron and steel industry which is responsible for up to 70 % of the total demand for refractories. During the use phase, 30 – 40 wt.% of the refractory is consumed, which then indicates that up to 28 million tonnes of spent refractories are generated every year [1]. In this paper, different processes which include usage of refractories, analysis of types of refractories, and their amounts will be discussed.

1.1. Historical evolution

Because there were concerns about chromium toxicity, spent-chrome containing refractories were the first to attract recycling attention. Hence, the initial research dated back to the early 1980s and the first patent concerned with reprocessing of spent magnesium-chrome bricks into refractory raw materials was published in 1985 [1]. Increasing environmental awareness and costs for waste disposal as well as decreasing the availability of space for landfills apparently influenced rising interest in recycling of these wastes. A decade later, this topic was not occupied only by regeneration regarding chrome-based spent refractories but also of other refractory types through the appearance of numerous patent applications published after the mid-90s (table 2). A larger study to identify recycling options and reduce landfilling, with related publications reporting on the characterization of spent refractories and development of recycling techniques was initiated also at this time, in the US.

The interest in recycling varies widely between countries and regions in relation to the local stress on resources and landfilling options. After the oil crisis in the 1970s, in Japan, recycling took a full swing, both in regards with study and application, while the examples of using the recycled refractories into the production of refractories were shown as early as 1999. At this time, reports have shown that almost 99 % of spent refractories have still been disposed at the landfills in the US, given that landfilling cost of most refractories was low, and that there were no true strong environmental or economic driving forces that could fight for the interest of refractory recycling. The different geographical interest and approach according to the refractory recycling is also evident from the relevant patent literature (table 2) [2]. Apart from a few European early filings in Germany, innovation is dominated by contributions particularly from Japan, and to a lesser extent Korea and China [1, 2].

Table 2. Number of patent filings of spent-refractory recycling during the interval of 5 years and by the country [1, 2]

	Canada	China	France	Germany	Japan	Korea	US	Total
1985–1989				1				1
1990–1994					2			2
1995–1999	1		2	3	3		1	10
2000–2004			1		11	1	1	14
2005–2009		6			11	1		18
2010–2014		20			8			28
2015–2016		10			2	2		14

2. CONCEPTS BEHIND THE RECYCLING OF WASTE REFRACTORY MATERIALS

2.1. 3 R's – Reduce, Reuse, Recycle

The 3 R's – Reduce, Reuse, Recycle (table 3) can be considered as a means to achieve zero emissions. "Reduce" would refer to the reduction of the consumption of refractories, in the way of decreasing the burden of furnace operations on the refractory lining. "Reuse" would mean the usage of waste refractories as slag modifiers and auxiliary raw materials. "Recycle" would mean reusing waste refractories as materials for furnace linings [3].

Table 3. Concept of 3 R's of spent refractories [2]

Reduce	• Relaxation of operating condition ⇒ Continuous operation, operation at lower temperature • Lifetime extension of refractories ⇒ High purity materials, optimum installation • Lifetime extension by reparing ⇒ Veneering repair, shotcrete, gunning
Reuse	Slag conditioners, raw materials used for refining, refractory sand, roadbed materials, etc.
Recycle	Reuse of SN plates, ladle shroud, spent brick, recycled products, landscape brick, unshaped refractories

2.2. The waste hierarchy

Due to environmental considerations and increasing costs for landfilling, recycling of spent refractories has started to receive more attention in the last two decades.

The waste hierarchy, as included in the latest version of the European Commission's Waste Framework Directive 2008/98/EC is described as a priority order for waste management options, with that being: 1) prevention, 2) preparing for reuse, 3) recycling, 4) other recovery (e.g. energy recovery) and 5) disposal [4]. One of the biggest shortcomings of the hierarchy is that it does not make a distinction between different types of recycling to maximize the inherent value of waste. In closed-loop recycling, the fundamental properties of the recycled material are not greatly different from those of the virgin material. The recycled material can in that case substitute virgin material and be used in identical products as before. In open-loop recycling, the inherent properties of the recycled material differ from those of the virgin material in a way that it is only suitable for use in other product applications, mostly substituting other materials [1].

The whole concept of waste hierarchy lies on the foundation of diverting waste from landfill. Figure 1 presents data on Domestic Material Consumption (DMC) and waste in the EU 27.

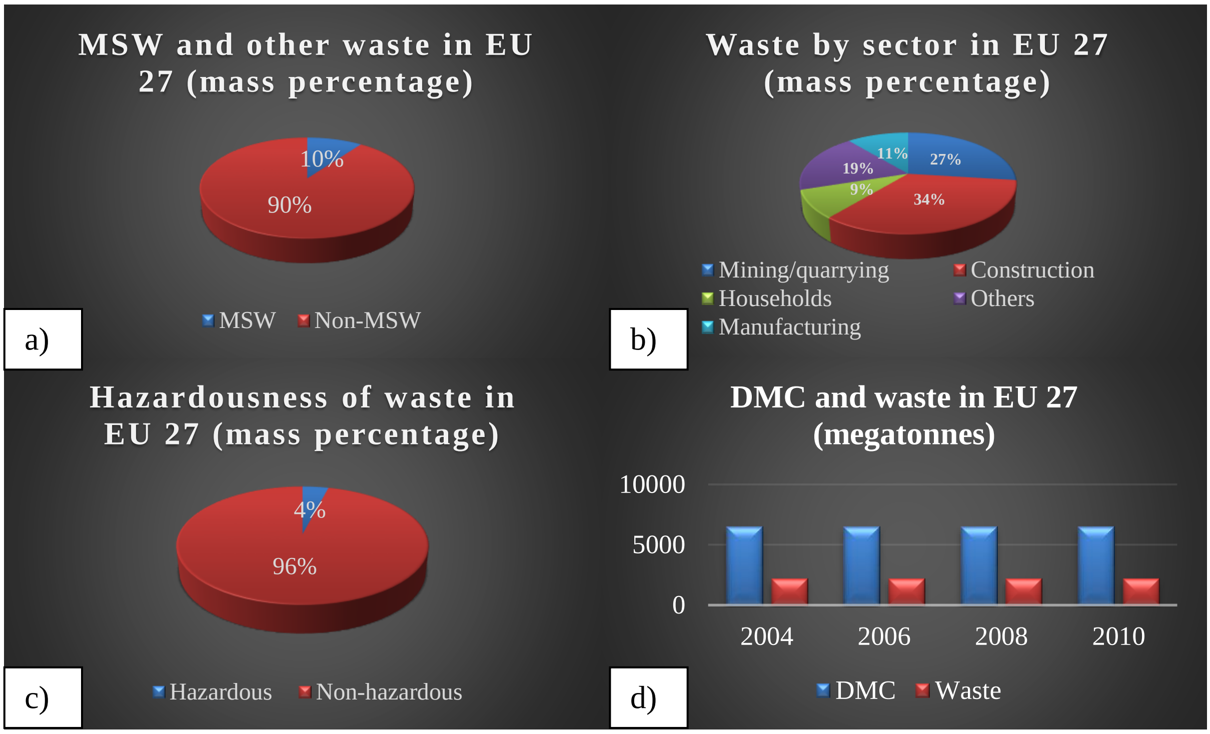

Figure 1. Domestic Material Consumption (DMC) and waste in the EU 27 in 2010 [4]

The sectors that happen to produce most waste are construction, mining, and quarrying (figure 1b) [4]. When the whole waste flow is considered, only about 4 % of the waste is actually hazardous waste (figure 1c), but most wastes have the potential to harm the environment (e.g., by causing biogeochemical imbalances, such as eutrophication).

Municipal Solid Waste (MSW), which is mostly household or domestic waste, is the most publicly noticeable sector. Even though it would be expected for MSW to have a bigger contribution in the total waste, the flow corresponds to only 10 % of the total waste flow and it even has a relatively low share of hazardous substances (Figure 1a) [4].

On figure 1d, the amount of waste as well as domestic material consumption, in megatonnes can be seen.

The waste hierarchy is a preferential order of waste treatment options that aims to reduce environmental impacts by prioritizing prevention, reuse, recycling, and recovery over landfill [4]. It is impossible to propose Hierarchy as countable for the development in waste management, but it can be claimed that transitions have been analysed in the Dutch waste sector through a variety of specific events and institutionalization processes. Be that as it may, it cannot be denied, that the waste hierarchy has had a large influence, as there was a consensus of support in most developed countries for the hierarchy to be a guide for waste management.

In the United States, there was attitude that landfilling untreated hazardous waste posed a potential threat to the environment and human health, from which the hierarchy rose. It was also claimed that the shift from disposal-based waste management to the hierarchy resulted from the three-fold waste crisis regarding cost, contamination and capacity in the 1980s [4].

Their ability to achieve diversion from landfill is a basic distinction between the alternatives, which is priority order. However, sticking to the waste hierarchy is also often equated with saving of resources and the least environmental impact. For example, the Waste Framework Directive (WFD) states that the "waste hierarchy generally lays down a priority order of what constitutes the best overall environmental option in waste legislation and policy" (EC. 2008). Also, a reduction of the use of resources as a policy goal is mentioned [4]. This paper should increase the understanding of the role of the hierarchy in the flows shown in figure 2. There are three different claims which have been made in regards with the waste hierarchy, which further relate in different ways to dematerializing of the economy. The first focuses on the diversion from landfill which further goes in favour of dematerialization, as it results in waste being recovered, recycled, or reused and therefore it comes as a substitute for virgin inputs. The second claims focus is on the reduction of environmental impacts as that is something which is also the main goal of dematerialization, but the waste hierarchy does not live up to this promise. Finally, the third one's focus is on saving resources by prioritizing recycling, reuse and recovery which does not guarantee dematerialization, as it reduces primary inputs but still allows secondary flows to grow unrestrained [4].

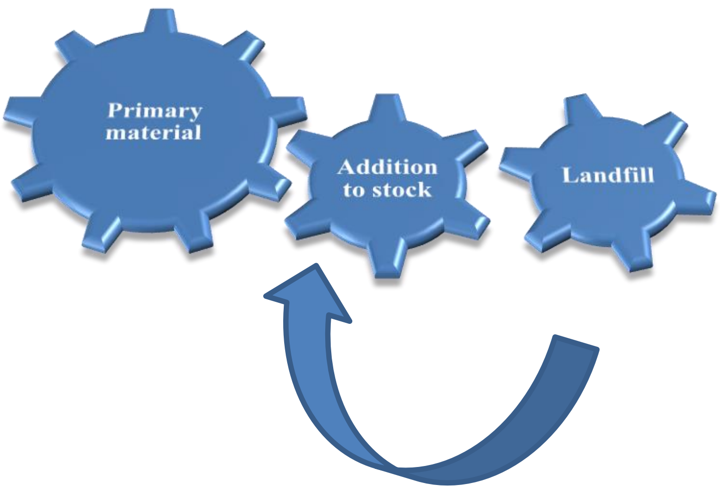

Figure 2. Basic material flows in economy [4]

At first glance, priority orders have great potential for policy making as they provide a seemingly clear-cut message on what needs to be done first [1]. However, a priority order implicitly judges the included options in three ways that may be counterproductive. Firstly, inclusion of an option in a priority order legitimizes its existence. For instance, instead of categorically rejecting landfill, the waste hierarchy states that other options are better than landfill. As such, it resides in between two extremes: on one hand approaches that accept landfill as a possible best option based on contextual factors, and on the other hand approaches that radically aim to achieve zero landfill, zero incineration, or zero waste. While the former promotes a workable outcome, the latter sends a clear message that may rally more support and achieve greater change. The waste hierarchy however, may fail to achieve either: there is no indication as to when landfill is an acceptable means, nor does it inspire radical change. The 3 R's concept may be better in this regard since it omits landfill [4].

3. REFRACTORY RECYCLING APPLICATIONS

3.1. Open-loop recycling of refractories

The most common application for spent refractory bricks is as roadbase aggregate. However, in order to avoid environmental impact, prior to use, leaching of heavy metals such as Cr, must be assessed. Pre-hydration is also something which is required to avoid expansion problems during use, especially for magnesia bricks. Doloma bricks are unsuited for this use due to rapid hydration and disintegration.

Basic bricks such as doloma and magnesia are commonly used as a conditioner or a slag former in metallurgical processes [1]. In order to reduce refractory attack, in Electric Arc Furnaces (EAF) metallurgical and dolomitic lime is added to increase MgO saturation of the slag. Provided that proper dosing is determined, replacing dolomitic lime with spent MgO-C refractory has led to higher MgO in slag and therefore increased refractory lifetime. Today the recycling of spent MgO-C refractory in EAF has been fully tested and implemented at industrial sites and is considered a recommended metallurgical practice. Using the spent refractories as slag conditioner has proven very beneficial, as it provides reduction or even complete eluding of landfilling, longer refractory lifetime, savings in fluxes and energy savings.

Spent magnesia-chrome refractories are recycled as scrap for production of chrome metals [1]. Doloma bricks in particular, are quick and effective soil neutralizers and have therefore been used in flowerbeds. Other applications are recycling as raw materials for clinker (cement) fabrication [1].

3.2. Closed-loop recycling of refractories

Although, open-loop recycling can be viewed as a valuable option to save virgin resources and reduce landfilling, recycling as raw materials to produce new refractories usually offers higher economic values. Furthermore, avoiding using virgin materials may result in significant greenhouse gas emissions savings, as well as significant energy savings. The production of magnesia (MgO) from its primary raw material magnesite ($MgCO_3$), can be a really energy intensive step, and the energy demand can be as high as 6 and 12 GJ/ton MgO which depends on characteristics and moisture content of the raw magnesite.

The process of recycling as raw materials can be complicated in practise, as it can result in a mixture of refractory materials, which can be hard to separate by grade and type.

The contamination which occurs during use can also pose a problem when it comes to meeting the high-quality demands for refractory raw materials.

Table 4 illustrates the difference in chemical composition between new and spent refractories [1].

Table 4. Average chemical composition of new and spent refractories [1]

Source	Refractory type		MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	C
Refrasort	MgO-C	new	96.2	1.3	0.7	0.8	0.9	11.0
		spent	94.5	1.8	0.9	1.1	1.3	10.0
	Fired MgO	new	97.0	0.8	0.4	1.3	0.4	0.1
		spent	90.0	2.0	1.5	1.5	3.5	
	Fired Doloma	new	39.0	59.0	1.0	0.5	1.0	
		spent	35.0	55.0	3.0	3.0	4.0	
	Doloma-C	new	39.0	58.0	0.6	0.6	0.9	5.3
		spent	37.0	59.0	0.7	1.4	1.3	4.6
	Fired Andalusite	new	0.3	< 0.15	0.9	59.0	38.0	
		spent	0.7	0.4	1.6	58.0	37.0	
	Fired Bauxite	new	0.5	0.5	1.4	83.0	10.0	
		spent	0.7	1.0	1.8	79.0	14.0	
	Fired Chamotte	new	0.5	< 0.15	1.3	43.0	53.0	
		spent	1.5		2.0	35.0	54.0	
	MgO-C (EAF)	new	84.7	< 1.2	< 0.5	< 0.5	< 0.5	12.7
		spent	86.1	3.6	4.7	0.7	1.7	15.3
ArianPour et. al. (2010)	MgO-C(ladle)	new	90.5	< 1.2	< 0.5	< 0.5	< 0.5	9.3
		spent	79.4	6.1	1.8	5.1	3.8	9.3
	MgO-C	new	90.7	1.7	0.7	0.8	0.7	18.2
		spent	74.2	2.8	0.5	1.6	1.3	17.2
Conejo et al. (2006)	MgO-C	new	85.0					10.0
		spent	85.1	3.8	0.3	0.3	1.0	8.0
	Doloma	new	35.0	60.0				n.s.
		spent	34.3	57.4	1.6	0.8	3.3	1.5
Smith et al. (1999)	Alumina Monolithic	new				92.0		
		spent	5.0	0.3	0.1	89.7	2.1	

n.s. not specified.

It can be seen that contact with the metal and slag during the refractory lifetime increases the amount of CaO, Fe_2O_3 and SiO_2 in the recycled refractories. The presence of these impurities typically results in a decrease of durability due to melt formation between Ca/Si and Mg/Al.

Furthermore, recycled refractory aggregates usually have higher porosity levels and lower density than virgin materials, and that affects the physicomechanical properties of the refractories as shown in table 5. Consequently, as the amount of recycled refractory aggregates, which can be introduced into the refractory mix, depends strongly on the purity of the recycled fraction, it is limited. Proper sorting and mineral processing is therefore required to obtain high quality raw materials [1].

Table 5. Physicomechanical properties of refractories produced with recycled aggregates [1]

Source		Addition of recycled aggregate,(%)	Bulk density, (g/cm^3)	Cold crushing strength, (N/mm^2)	Apparent porosity, (%)
REFRASORT	MgO-C brick	0	2.91	30	11.1
		30	2.86	27	12.5
		50	2.84	26	13.1
		80	2.77	21	14.3
Arianpour et.al. (2010)	MgO brick	0	2.95	45.2	16.2
		10	2.85	38.5	18.5
		20	2.85	38.2	18.5
		30	2.43	36	20
	MgO ramming mix	0	2.85	39	25
		10	2.8	34	27
		20	2.78	30.5	31
		30	2.6	37	31.5

4. REFRACTORY RECYCLING

After the refractories have completed their lifetime, they should be disposed of or as mentioned already they should be subjected to the recycling process. It can be seen on figure 3 how this can be done. In the last two decades, the refractory industry has significantly favorized recycling thus minimizing the damage to the environment, but also the reduction of the implementation costs. Research has shown that there is no real difference between the thermal stability of the newly produced refractory materials and the converted ones [1]. Thanks to the latest techniques being developed in terms of recycling methods, this process is easier and more efficient than ever before.

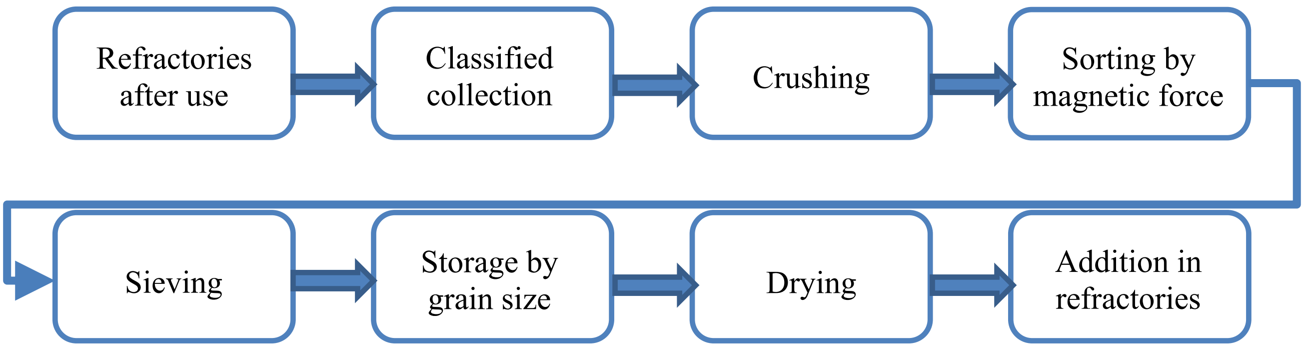

Figure 3. Recycling process of refractories [4]

Depending on the structure and nature of the material, the recycling process of refractory materials can vary [5]. If for example, a furnace gets disassembled, there will be a lot of different parts that would need to be subjected to the recycling process. It is evident that there is no possibility to apply the same recycling treatment for all of the parts. Therefore, the first thing that needs to be done is to make a distinction between the waste refractories based on the categories. Carbon refractories, MgO refractories and carbonless refractory materials are an example of this distinction [1]. As iron and slag can be found with different rates in each of the components, this is something that can provoke a certain problem during the recycling procedure and therefore raises a concern.

The first thing that needs to be done is to separate iron, slag and other materials from one another. This process can be accomplished manually, as well as by magnetic methods which are more often the case. After this step, the refractory material is pulverized. For this process (depending on the type of material) heating, pressure or milling methods can be used. The aim is to attempt recovering the characteristics of the refractories into the initial and pure form. In order to avoid exposure to moisture and dust, all necessary protection measures must be taken [5]. Recycling of the refractories is a process that is important in many respects. Monthly production of refractory waste in an average steel factory is around 4100 tones. With an efficient plan and process of recycling in place, a portion close to 40 % of refractory wastes can potentially be preserved and re-used in the industry. Thus, it would be possible to reduce the operating costs remarkably as well as the damage to the environment [1].

If the chemical composition is well known, and if the quality can be guaranteed then recycling as raw materials can be done for different refractory types, without the loss of functionality. Because of this, there is a strong need for a sorting and pre-treatment.

A new and up-to-date recycling plant for refractory waste should most commonly include at least two steps. The first step includes pre-sorting of the refractory waste based on the refractory type. After the first step, different types of refractory materials are still mixed and contaminated with huge pieces of iron metal and slag material. The pre-sorting is mostly done manually. The second step therefore consists of further, mostly automated, treatment of the pre-sorted refractory streams by e.g. crushing, screening, magnetic separation and colour separation with the aim to remove impurities such as iron, slag, and unwanted pieces of refractory material [1].

Through the development of the process, attention was mostly on upgrading the second step, namely purification. In the recent years, evidence of shifting attention to the first step can be seen, with an aim to automate it.

5. BARRIES FOR REFRACTORY RECYCLING AND WAYS TO OVERCOME THEM

Recycling of spent refractories in new refractory production has been proven technically feasible. Although, recycling of some types of refractories, like MgO-C, has been a common practise for more than a decade, recycled refractories still only make up 7 % of the raw materials input. One of the major issues is the quality assurance and cost competitiveness of the recycled products [1]. In order to have an operational production, a long term adequate and stable supply of consistently high quality secondary raw materials must be provided. On the other hand, problems arise because of the belief of the refractory producers that the recycled materials should be considerably cheaper than virgin materials, due to the expected lower quality and higher risk. Within the current circumstances, the only feasible solution is to recycle merely the highest quality, easy to sort refractories such as MgO-C, which make up a minor fraction of the total volume. The low disposal costs for this type of material (except for Cr-containing bricks), and the small amounts of refractory waste per factory further limit the economic viability [1].

Other threats to refractory recycling are lack of clarity and consistency of legislation regarding handling, treatment and transport of waste materials across country borders, and the administrative burden [1].

Technical advances are a sure bet to overcome these threats. Automated sorting, for example, has the potential to make the recycling process cheaper and more reliable, resulting in higher and better quality. Such a system would also be able to deal with more diverse input streams, without any prior knowledge, and it would enable pooling of different sources to attain critical mass. As such, these systems would greatly improve the cost competitiveness of refractory recycling.

Purity of the spent refractories is another aspect of the process that would require further attention. It could be greatly enhanced even before processing by selective demolition of the refractories at end of life.

Higher purity has a strong positive impact on the recycling rate, as it allows a higher proportion of recycled fractions to be added to the refractory mix. However, to avoid risks, there is a tendency in the industry to use only the highest quality of well-known recyclates, even though lower quality material would suffice. Refractory types that are not commonly recycled today should be used to achieve the full potential of recycling. This requires cooperation between the refractory production and processing industry to develop new formulations and demonstrate their reliance in the field [6].

6. CONCLUSION

Refractory production is heavily relying on high quality raw materials, many of which are becoming increasingly difficult to come by, and prices are rising. A whopping amount of up to 28 million tons of spent refractories is being generated each year, with only a small fraction of it being recycled in refractories. Although recycling of refractories took up two decades ago, in the beginning it was mostly focused on reducing waste and associated landfilling costs. Because of the possible benefits, both economical (cheaper raw materials, lower treatment costs) and environmental (lower energy demand and CO_2 emissions compared to virgin materials), high value recycling in new refractories has gathered pace. Even though such reuse has been proven technically feasible, it has actually only been used for a limited number of refractory types such as MgO-C.

The main problem is the quality assurance of the recycled fractions, which is deeply dependent on proper sorting of spent refractories. The most cutting edge technology in recycling industry is manual sorting and it is quite error prone and it requires prior knowledge. This can cause an effect which could limit the amount of well-sorted fractions that are available on the market as it could inspire an alarmed attitude from possible buyers.

Technical advances such as automated sorting have the potential to increase both the quality and availability of recycled refractories, but require further development and investments [7]. A change in mindset is also due as end producers need to accept refractories produced with recycled materials as a valid option.

Even then, regardless of the quality of the sorted fraction, some refractory types will probably remain unsuitable for recycling in refractories due to technical issues (e.g. hydration of doloma) or low value (e.g. chamotte). In order to improve the overall economics of the recycling process, and optimize the material balance, such materials will still have to be used in applications outside the refractory production industry, such as road bed aggregates or fluxes [4].

While one could argue if this is evident, the current situation in Europe provides strong incentives for the industry. Since the European industry is aware of the strong dependence on import, and the potential supply risks, owing to recent evolutions in the market, with rising costs and price volatility of virgin raw materials. In 2008 the European

Commission adopted the Raw Materials Initiative which is built on three principles. One of them is focused on recycling and through it, achieving resource efficiency and supply of secondary raw materials as it recognises the importance of access to raw materials. This one as well as other related policy actions should improve and raise research and innovation in the field of raw material recycling in general, and they are proving to be an excellent opportunity for the further development of refractory recycling in particular [4].

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