# Refractory Raw Materials from the Steel Industry

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About 70 % of all refractory products are used in the steel industry. When they are spent, they can be a valuable source of raw materials. Therefore it is necessary, to sort the waste and recycle it. The authors want to show, how this is done by *Horn & Co. Group*.
The different areas of a steel mill are considered, what materials are used, how they are processed and which secondary raw materials are produced from. Using the example of some of their derivative products, the suitability of these regenerates is shown and their cost advantages will be outlined.

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## 1 Refractory raw materials become more and more expensive and scarce

The demand for high-grade materials as well as market availability and pricing policy of suppliers are reasons for the rise in prices. Since the millenium turn, the following development can be observed (Fig. 1). A closer look at the raw materials is shown in Fig. 2.
With the exception of clay, these materials are scarce; the production of the synthetic raw materials requires plenty of energy and is expensive, therefore.
The main deposits of bauxite containing less than 2 % of ferric oxide are located in China and Guayana (in both cases property of Chinese companies). China has also 27 % of the worldwide magnesite stocks at its disposal (North Korea 24 %, Russia 22 %) and Slovakia 12 % [3].
Replacement of raw materials (for example, bauxite by andalusite or fireclay) or use of recycled raw materials are alternative options to substitute the more and more expensive and scarce raw materials. Here a closer look at the second possibility of these options is given.

## 2 Steel industry – a source for refractory materials

The steel industry requires approximately 70 % of all refractory materials. Therefore it should also be the biggest source for used materials. Really, the steel mills always found and continue to find simple ways to rework and put used materials in work again.
However, it was only the development in the recent 20, 30 years that led to the insight that consumers may address the steel industry as a raw material supplier and that such utilization should become not only a local solution. On the example of the *Horn & Co. Group* (Siegen/DE) described the extent achieved and the course followed on this way.
In *Mineralmahlwerk Westerwald* (a part of this group) more than 150 000 t of used refractory materials are reworked per year. As

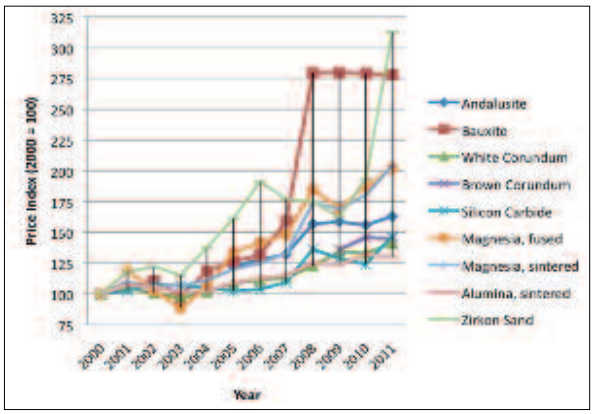


**Fig. 1** Development of costs of refractory raw material [1]

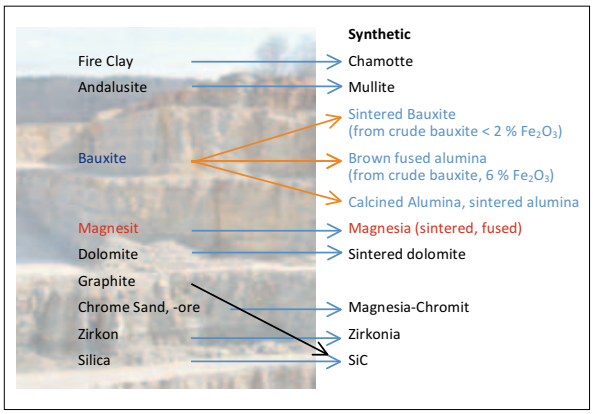


**Fig. 2** Main raw materials [2]

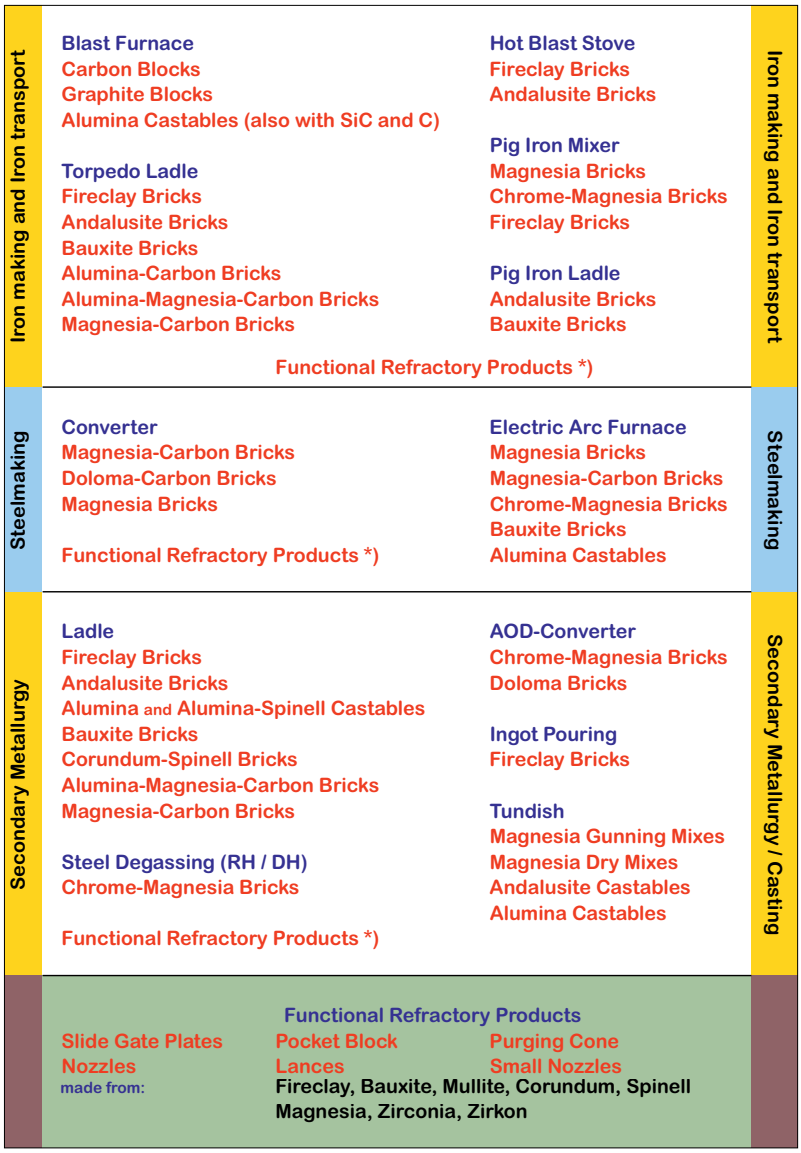


**Fig. 3** Aggregate/plant, refractories

raw materials, they are sold to major European refractory producers or used for the own production. The main portion of them comes from the steel industry. The sources are shown in the survey (Fig. 3).

How are the residual materials treated in order to make safe-quality raw materials from them?

In collaboration with the steel mills, a possibly best way is agreed for each material. The refractory breaks have to be collected in dependence of origin and put in intermediary storage. They should not be mixed with other materials. If possible, first sorting should be done still on the spot. Some steel mills do this themselves or give the task to other companies. In eight German steel mills this is done by employees of the Horn & Co. group. If the quantity of refractory waste is too low (less than 2000 t) also the materials on one of the central sites in Germany, Sweden, Luxembourg, or Poland are taken over.

## 3 Treatment of the refractory breaks

Sorting and cleaning should always ensure an exactly graded product of the further treatment as raw material. On the sorting equipment, experienced employees assess each brick, sort the material in accordance with its composition and remove adhering slag, visible infiltrations, and other impurities from it. In many cases it is purposeful to screen the material before sorting (Fig. 4).

Colour, lustre, grain shape, brick size, fracture system, and odour are differentiation criteria. There are comparative reference materials for safe assessment, and analyses in each reworking phase have been stipulated to assure quality.

As the visual differentiation of carbon-containing bricks is often difficult, latest modern analytical methods are applied. Each brick is measured and the result of the analyses is displayed. The adequate measuring method was already presented on the International Refractory Colloquium in Aachen in 2008 [4]. In the meantime it has been perfected (Fig. 5).

Depending on customers' wishes, further reworking is made by breaking, drying, grinding, screening, blending, and packing. Each

**Fig. 4** Sieving and sorting devices

raw material produced in this way is equipped with a quality certificate.
A centralized reworking can provide further advantages because there are different types of crushing devices available or if the portion of disturbing magnetic matters (iron, slag) can be reduced by magnet separation. Moreover, it is possible to make purposeful use of a concentration of some components in certain grain fractions.

## 4 Types of refractory raw materials made from spent materials

The survey (Fig. 6) of the most important material types reworked by Mineralmahlwerk Westerwald shows the diversity of raw materials and their origin. Really, most of the materials reworked are bricks and fused materials, but concretes are suitable for recycling as well in some cases.
The price level of the different processed materials is in the range of about 60 to 100 % of the respective primary raw materials. Sorting, transport and further treatment are cost factors and not to forget the cost of procurement of the breaks in the steel mills.

## 5 Peculiarities of the use of recycled refractory raw materials

When reworked materials are selected and used, some peculiarities should be observed because the material is nearly always subject to changes in use and small impurities may still occur, in spite of careful reworking. It is seldom possible to substitute a primary raw material in a 1:1 ratio. As for all other raw materials, properties are decisive for the possible use. So, grain shapes may be quite otherwise, porosity is often higher, and density sometimes somewhat lower than for the primary raw material. However, quite new combinations are possible as well. For example, it is possible to use regenerated bauxite for the production of an andalusite brick.
The quality of high-grade Magnesia R is for example even better than that of common Chinese sintered magnesite with 90 % of MgO. Therefore, the gunning mixtures for arc furnaces made from Magnesia R are characterized by best lifetime values (Tab. 1).
Another example describes a further general peculiarity of many reworked raw materials. As in use the material is often still subject to important changes (recrystallization, forming


**Fig. 5** Determination of composition

| Description | Basis | Remark |
|---|---|---|
| Mag-Carbon R 90A6 | Mag-Carbon bricks | standard grade |
| Mag-Carbon R 92A2 | Mag-Carbon bricks | low $Al_2O_3$ |
| Mag-Carbon R 86A9 | Mag-Carbon bricks | with antioxidants |
| AMC R | Alumag-Carbon bricks | |
| Magnesia R | Magnesia bricks and wear lining tundish | different grades (MgO 80 – 95 %) |
| Magnesia-Chromit R | Magnesia-Cromite bricks | two grades |
| Alu-Carbon R 77 | Alu-Carbon bricks | |
| Alu-Carbon R 82Z6 | sliding gate plates | |
| ASC R 68 | concrete from blast furnace runners | |
| Andalusit R | Andalusite/Sillimanite bricks | different grades |
| Bauxit R | Bauxite bricks | two grades |
| Alu-Carbon R 79 | Alu-Carbon bricks and sliding gate plates | a blend of different materials |
| Schamotte R | Chamotte bricks | different grades $Al_2O_3$ 30 – 45 % |
| Forsterit R | Forsterite bricks | |
| Dolomit R | Dolomite bricks | different grades |
| Other grades from other industries (nonferrous metallurgy, glass, cement, lime, chemicals) | | |
| AZS R Z35 | Corhart-ZAC blocks | different grades |
| AZS R Z30N4 | Corundum-Zircon bricks | |
| Magnesia-Spinell R | Magnesia-Spinell bricks | different grades |
| Magnesia-Zirkon R 75Z9 | Magnesia-Zircon bricks | |
| Mullit R | Mullite bricks | |

**Fig. 6** Types of refractory raw materials made from spent materials

of new phases, coking), the reworked material will also have other properties than the primary raw material. So, for andalusite bricks made from pig-iron transfer ladles the phase composition changes in use (formation of mullite) (Fig. 7).
Similarly to primary raw materials, one should know the properties of reworked materials as well as possible. Then disadvantages can be avoided whereas benefits can be used.

As a summary, it can be said that the steel industry, being the biggest consumer, is also an important source for used refractory materials and the dependence on raw-material suppliers, especially from China, can be reduced. Greenness is another very significant point, because – besides the elimination of the long transportation ways for bauxite, magnesite, or ready-made products from China to Europe – reworked materials usually do not require calcination or firing. The

**Tab. 1** Analysis of primary sintered magnesite and reworked Magnesia R

| | MgO [%] | CaO [%] | $SiO_2$ [%] | $Al_2O_3$ [%] | $Fe_2O_3$ [%] |
|---|---|---|---|---|---|
| **DB sintered magnesite (China)** | 90,80 | 2,95 | 3,67 | 0,47 | 1,60 |
| **Magnesia R (Horn & Co.)** | 93,50 | 1,60 | 2,29 | 0,52 | 0,43 |

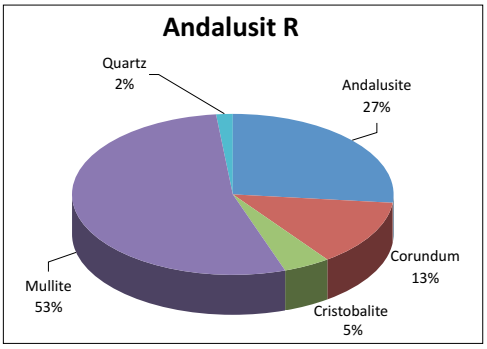


**Fig. 7** Andalusit R – mineralogical composition

positive effect consists in a reduced load of the atmosphere with $CO_2$ greenhouse gas. For a further increasing application of regenerated used refractory materials it is necessary to equip all participants with the required knowledge of how to rework high-grade secondary raw materials. For many companies this is still a novelty. So they have to learn and change their views, design new processes, develop innovative products, test secondary raw materials and new recipes, and find suitable applications.

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