Recovery of spent refractories: how to do it and using them as secondary raw materials for refractory applications

Serena Fasolini, Michele Martino – DEREF SPA, Genoa Italy

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DEREF presentation
Company profile

Head office: Genova, Italia

Production plants:
Castiglione in Teverina (VT), Pisa (PI), Terni (TR), Vignole Borbera (AL).

Area of activity:
EU (Italia, Belgium, France, Germany, Spain, Greece, Slovenia...), Serbia, Turkey, Switzerland, United States...

Turnover: 12 M€ (2015)
Workforce: 40 people
Production: 60 000 t (2015)
Locations

Genova
Head Office
Administration
Purchasing Dept.
Commercial Dept.

Vignole Borbera
Refractory Plant
Selection of refractory material
Warehouse

Pisa
Refractory Plant
Selection of refractory material
Warehouse

Castiglione
Refractory Plant
Spray Dry Plant
Kieselsuhr Plant
## Main activities

<table>
<thead>
<tr>
<th>Demolition and Recovery of Refractory Materials</th>
<th>Industrial Minerals Production &amp; Sales</th>
<th>Products for Steel Industry</th>
<th>Production of Kieselguhr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demolition</td>
<td>Raw materials</td>
<td>Refractory granulate for EAF</td>
<td>Natural Kieselguhr</td>
</tr>
<tr>
<td>Refractory Material Recovery</td>
<td>Secondary raw materials</td>
<td>Fluidifying and desulfurization</td>
<td>Calcined Kieselguhr</td>
</tr>
<tr>
<td>Services</td>
<td>Services</td>
<td>Covering powders</td>
<td>Filter aids</td>
</tr>
</tbody>
</table>

Derief is specialized in the demolition of refractory linings of industrial furnaces in the fields of glass, ceramic, cement, lime and steel. The demolished scrap then undergoes an upgrading process through Derief's treatment plants.

Derief produces and places on the market a wide range of mineral raw materials which are employed for shaped and non-shaped refractory materials intended for steel, tile and glass markets. Derief is a leader company at European level for manufacturing of secondary raw materials.

Derief produces a wide range of mineral products covering applications in the whole production cycle of steel plants, from the electric furnace to slag treatment. Derief is one of the main manufacturers of spray-dried insulating powders.

Derief produces Kieselguhr, of natural and calcined type, employed in chemical and food industries. The Kieselguhr derives from the diatomaceous earth extracted from quarries directly owned by Derief and located in the central part of Italy (Viterbo province).
Demolition and recovery of refractory materials

Demolition of glass furnaces
In situ treatment of steel production refractory scraps
Recovery of refractory scraps from different industries
Demolition and recovery of refractory materials

Origin of refractory scraps

- Steel industry: 61%
- Glass industry: 27%
- Ceramic: 6%
- Various: 6%

Deref
Demolition and recovery of refractory materials

Materials application

- Steel industry: 69%
- Refractory: 18%
- Ceramic: 11%
- Various: 2%

Deref
The recovery and the treatment of spent refractories
Demolition and recovery of refractory materials

Steel industry

- Regular collection
- Few qualities, important quantities
Demolition and recovery of refractory materials

Magnetic and non magnetic (stainless steel) metals

Slag, dust and carbon contents

Refractory materials with phosphate binders or anti oxidant components
Demolition and recovery of refractory materials

Glass industry
- 500 / 5000 t each furnace
- up to 40 qualities of refractory materials
Demolition and recovery of refractory materials

Tank: presence of glass and sodium absorption, metallic inclusions (iron, Pb, Sb...), refractory containing chrome oxide...

Superstructure: sodium absorption, crystallographic transformation...

Regenerators: sulphates, borates and heavy metals pollution (Pb, Ni, V, As, Se...)
Demolition and recovery of refractory materials

Cement and ceramic industry

Small quantities, regular quality = high value of scraps

Unfired products
Recovery of refractory materials

Origin of refractory scraps used for refractory applications

- Steel industry: 46%
- Glass industry: 30%
- Ceramic: 14%
- Various: 10%

Deref
Production of secondary raw materials for refractory applications
Production of secondary raw materials

Process

- Selezion / Sorting
- Frantumazione / Crushing
- Stoccaggio / Storage
- Macinazione secondaria / Secondary grinding
- Deterizzazione / Iron removing
- Classificazione / Screening
- Campionatura / Sampling
- Imballaggio / Packaging
- Analisi / Analysis

Materie prime secondarie / Secondary raw material
Materie prime vergini / Virgin raw material
Production of secondary raw materials

Pre-selection

Management by origin and batch

Classification by quality, for ex. : AZS
- new, cleaned, semi cleaned, dirty
- soda glass, borosilicate glass, float glass, special glass (ceramic glasses, fiber, crystal, optical...)
- from tank, from superstructure, from bottom layer

Furnace and refractory data sheets collection
Production of secondary raw materials

**Sorting**

- Screening of fine parts
- Manual sorting
Production of secondary raw materials

Sorting

![Image 1](image1)
![Image 2](image2)

![Image 3](image3)
![Image 4](image4)
Production of secondary raw materials

Cleaning and intermediate processes

Mechanical and manual physical processes

- Classification by quality,
- separation of glass
- separation of non suitable parts
- iron removing
- drying
Production of secondary raw materials

Grinding and screening

Multi step crushing and grinding with jaw and cone crushers and roller mills

Standard grain sizes
0/50 mm
0/8 mm
0/1/3/6 mm
0/0,5/2/5 mm
Production of secondary raw materials

**Packaging**

Standard
- In bulk
- 1500 kg big bags with plastic cap

Special
- 25 kg paper bags on pallet
Production of secondary raw materials

Quality management

Know-how of the product: origin, treatment, crystallography, chemistry, density and porosity, availability

Complete control of the production process

Know-how of the application: critical parameters.

=> TDS sharing between producer and user.

Quality control:

- Size control, Water content
- Firing tests
- Chemical (XRF) and crystallographic analysis (XRD)
Quality management

Production procedures

Sampling: dedicated procedures

The Producer carries out physical analysis, chemical, and mineralogical control

End users carry out reception control and give feedback on use
Secondary raw materials for refractories
The use of secondary raw materials

Relevant figures

In Italy, **80 000 t/year** of spent refractory materials are recycled in the different production sectors that use refractory materials in the plants (Glass, Cement, and Ceramics Factories, non-ferrous Metallurgists, Petrochemical, etc.)

The breakdown of re-use of this huge quantity in the various fields of application can be summarised as follows:

- Refractory industries 40 - 45 %
- Steel making processes 35 - 40 %
- Other applications 5 - 10 %
- Not re-used, waste < 10 %
The use of secondary raw materials

General requirement

In order to take advantage of the potential benefits of the recycling, the following conditions are absolutely essential:

- **Correct recovery and treatment** of scrap refractory materials

- **Good knowledge of the recycled raw materials**, the advantages and criticalities associated with them and, consequently, the correct formulation of refractory products that contain them, in relation to the type of refractory situation in which they are used and the forces they will be subjected to.
The use of secondary raw materials

Secondary chamotte

Using these recycled raw materials is relatively simple, also in view of the refractory items usually made using them.

For example:
- Castables, rammings, plastics and gunnings for general use
- Fired fireclay for general use

The replacement percentages range from 10-15% to as high as 80%
The use of secondary raw materials

Secondary chamotte

The criticalities to be taken into account relate mainly to monolithic items and can involve:

- The porosity of the raw materials, which can have a great impact on the water requirement and, as a result, the binding and physical mechanical characteristics.
- The presence of high pH salts that has a direct effect on the casting and binding characteristics.
- High porosity calls for a lot of wetting liquid for ramming and plastics, resulting in a weakening of the characteristics.

The use in fired fireclay is much less problematic, where a good refractory operator can balance the product by adding a clay binder and adapting the firing cycle.
The use of secondary raw materials

Recycled mullitic chamotte

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical properties</td>
<td></td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>% 55 - 65</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>% 30 - 40</td>
</tr>
<tr>
<td>( \text{CaO} )</td>
<td>% 2 - 10</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>% 1 - 3</td>
</tr>
<tr>
<td>( \text{MgO} + \text{CaO} )</td>
<td>% (&lt; 1)</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} + \text{Na}_2\text{O} )</td>
<td>% (&lt; 1)</td>
</tr>
<tr>
<td>Water content</td>
<td>% max. 1</td>
</tr>
<tr>
<td>Density</td>
<td>( \text{g/cm}^3 ) 2.4</td>
</tr>
</tbody>
</table>

The chemical analysis relative to the oxides is reported on the calcined.

Main crystallographic phases: mullite.

<table>
<thead>
<tr>
<th>Grades</th>
<th>Packaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncrushed, 0/1 - 1/3 - 3/6 mm</td>
<td>Big bag 1500 kg with pallet</td>
</tr>
<tr>
<td>Other grain size available for complete lining</td>
<td>Bulk</td>
</tr>
</tbody>
</table>
The use of secondary raw materials

Recycled mullitic chamotte

This group of recycled raw materials plays an important role in manufacturing medium alumina content refractory materials, for both shaped and monolithic products.

Besides the alumina content, careful examination of the mineral composition is important: it can be derived from both mullitic chamotte and andalusite based products transformed to varying degrees in firing and/or operation.
The use of secondary raw materials

Recycled mullitic chamotte

Clearly, depending on their mineral content both the areas of use and the composition parameters of the refractory item to be produced must vary:

- Those derived from andalusite or mullitic chamotte, basically all transformed into mullite, are used for both shaped and monolithic products as a replacement for primary mullitic chamotte. Generally the percentage replacement ranges from 20% to 60% depending on the quality level required.

- Those that still have a significant andalusite content are used as a partial replacement of andalusite itself. In this case, during product formulation, the expansion / shrinkage of the material must be examined in comparison with the original, due to the well-known secondary expansion of andalusite and, if necessary, suitable compensatory additives must be used.

When using monolithic elements, it is essential to take into account the possible criticalities examined in the previous case.
The use of secondary raw materials

Sinter and EF recycled mullite

<table>
<thead>
<tr>
<th>DER MU 75</th>
<th>DER MU EF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sintered Mullite</strong></td>
<td><strong>White Fused Mullite</strong></td>
</tr>
<tr>
<td><strong>Chemical properties</strong></td>
<td><strong>Chemical properties</strong></td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al}_2\text{O}_3 )</td>
</tr>
<tr>
<td>( % )</td>
<td>( % )</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>( % )</td>
</tr>
<tr>
<td>( % )</td>
<td>( % )</td>
</tr>
<tr>
<td>( \text{CaO} + \text{MgO} )</td>
<td>( % )</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} + \text{K}_2\text{O} )</td>
<td>( % )</td>
</tr>
<tr>
<td><strong>Water content</strong></td>
<td><strong>Chemical properties</strong></td>
</tr>
<tr>
<td>Density</td>
<td>( % )</td>
</tr>
<tr>
<td>( \text{g/cm}^3 )</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Physical properties</strong></td>
<td><strong>Physical properties</strong></td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>( % )</td>
</tr>
<tr>
<td>( \text{g/cm}^3 )</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Packaging</strong></td>
<td><strong>Grades</strong></td>
</tr>
<tr>
<td>Dry bag 1500 kg on pallet</td>
<td>( \text{g} ) &amp; ( \text{cm}^3 )</td>
</tr>
<tr>
<td>Rig bag 1500 kg with pallet</td>
<td>0.5 - 0.6</td>
</tr>
<tr>
<td>Other grain size available for complete furnaces</td>
<td>0.7 - 0.8</td>
</tr>
<tr>
<td>Other grain size available for complete furnaces</td>
<td>0.9 - 1.0</td>
</tr>
</tbody>
</table>

**Notes:**
- \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) contents are within the specified range for optimal performance.
- The water content is kept to a minimum to ensure product integrity.
- The density is critical for applications requiring compact materials.
- Packaging options are provided for convenient handling and transportation.

**Deref**
The use of secondary raw materials

Sinter and EF recycled mullite

These are noble recycled raw materials due to their origin and possible use, normally available in limited quantities, and they stand out mainly due to the nature of the original raw material (sinter or EF), and so the product from which they are derived must be carefully evaluated (shaped, fired or prefabricated with hydraulic bonding).

In the second case, use falls into the group of the products of origin, with due care taken over the criticalities already indicated, whereas in the latter the prime use is in high class, high performance fired shaped items.

Deref
The use of secondary raw materials

Recycled bauxite

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>% 55 - 72</td>
</tr>
<tr>
<td>(Typical)</td>
<td>70</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>% 20 - 24</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>% 3</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>% 2</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water content, % max</td>
</tr>
<tr>
<td></td>
<td>Density, g/cm$^3$</td>
</tr>
</tbody>
</table>

The chemical analysis relative to the samples is reported on the following:

Main crystallographic phases: mullite, corundum

Grades:

- 0/0.5 - 0.5/2 - 2/8 mm
- 0/1 - 1/2 - 3/8 mm

Other grain size available for complete lorry

Packaging:

- Big bag 1600 kg with pallet
- Bulk

Deref
The use of secondary raw materials

Recycled bauxite

This group includes recycled raw materials derived from greatly varying origins and compositions and that, therefore, call for careful preliminary evaluation, in order to define possible fields and contents for use.

The major origins can be summarised as follows:

- A) Fired, Bauxite-based, shaped products with possible varying additives and variable Al$_2$O$_3$ content.
- B) Chemically bonded Bauxite-based, shaped (generally phosphates), bonded with a variable Al$_2$O$_3$ content.
- C) Bauxite-based prefabricated products with a hydraulic binder.
The use of secondary raw materials

Recycled bauxite

Use of these can differ according to the origin, although in general one can define:

- For group A) materials: All-purpose type raw material, which can be used in shaped and monolithic products in variable percentages according to the alumina content and any casting criticalities for unshaped items.

- For group B) materials: Use of this raw material is not recommended for monolithic items due to the reactions the phosphate salts have in terms of their rheology, grip and characteristics. These can be used for chemically bonded shaped items, as well as for fired items, bearing in mind their behaviour in relation to sintering.

- For group C) materials: Use of these materials is basically limited to the group of products of origin, and their overall chemistry must be considered carefully. They are also used in non-refractory settings.
The use of secondary raw materials

Recycled high alumina materials

![Image of recycled high alumina materials]

**DER A90 C**

*High Alumina Ceramic material*

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th>Physical Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>%</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>% min</td>
</tr>
<tr>
<td>( \text{CaO} + \text{MgO} )</td>
<td>%</td>
</tr>
<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>%</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>%</td>
</tr>
<tr>
<td><strong>Water content</strong></td>
<td>% max</td>
</tr>
<tr>
<td><strong>Spec. Weight</strong></td>
<td>g/cm(^3)</td>
</tr>
</tbody>
</table>

The chemical analysis of oxides is referred to the calcined product.

**Grain size**: Un-crushed 0-160 mm.

**Packaging**: Bulk or big bag on pallet.

![Logo of Deref]
The use of secondary raw materials

**Recycled high alumina materials**

For this type of raw material it is important to determine their origin beforehand and, consequently, their characteristics and possible fields of use. In very simple terms:

- Derived from refractory material recovered from plates for a ladle sliding gate (generally impregnated with pitch)
- Derived from special items supplied in steel mills (purging plug block, sleeves, other special items) for which a distinction must be made between ceramically bonded materials and hydraulically bonded materials.
- Derived from electro-fused alumina blocks used in both steel mills (e.g. reheating furnaces) and in glass making industry.
- Derived from other industries, especially from technical type ceramics and the petrochemical industry.
The use of secondary raw materials

Recycled high alumina materials

Since the origin of these is so varied, the possible uses also vary and are also summarised here by way of example:

- Recycled raw materials derived from sliding gates (almost always with an alumina slab base, with possible mullite and/or zirconium content) are excellent, with the sole limitation of the inclusion of impregnation pitch. Given the high cost (also in ecological terms) of calcination of these materials, they are normally used for feeding both shaped and unshaped refractory items that contain carbon into the formula. For example, the latter include tempered products in the $\text{Al}_2\text{O}_3$-$\text{SiC}$-$\text{C}$ and $\text{Al}_2\text{O}_3$-$\text{MgO}$-$\text{C}$ groups.

- High Alumina materials without carbon (i.e. purging plug blocks) obviously have a much more general field of application, even though quantities are generally not very large. However, the rule that material derived from hydraulically bonded products must be used for the same purpose must always be observed.
The use of secondary raw materials

Recycled high alumina materials

- Provided they are properly selected and screened, materials derived from electro-fused blocks can easily replace part or all of the virgin electro-fused corundum, both white and brown fused, according to the chemical profile obtained.

- As for recycled raw materials derived from other industries (ceramics, technical ceramics, petrochemical, etc.), the definition of the fields of use depends mainly on their chemical profile. In general, those derived from technical ceramics have an excellent chemical profile, do not contain components that melt at low temperatures, have high density, and almost zero porosity and can therefore be used as high performance refractory components. For the others, once any melting components have been checked for, as well as the quantity of each of them, use can be established according to the maximum operating temperature of the finished product.
The use of secondary raw materials

Carbon magnesite

DER MGO-C
High grade secondary carbon magnesia (electrotused and sintered magnesia from CaO and MgO)

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MgO</strong></td>
<td>%</td>
</tr>
<tr>
<td><strong>MgO</strong></td>
<td>% min</td>
</tr>
<tr>
<td><strong>Fe₂O₃</strong></td>
<td>%</td>
</tr>
<tr>
<td><strong>Al₂O₃</strong></td>
<td>%</td>
</tr>
<tr>
<td><strong>SiO₂</strong></td>
<td>%</td>
</tr>
<tr>
<td><strong>Water content</strong></td>
<td>% max</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>g/cm³</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grains</th>
<th>Packaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 mm</td>
<td>in bulk</td>
</tr>
<tr>
<td>Crushed 0.50 mm</td>
<td>Big bag 1500 kg</td>
</tr>
</tbody>
</table>

The chemical analysis on evities is to be referred to calculated products.
The use of secondary raw materials

Carbon magnesite

This recycled raw material has become strategic for European carbon magnesia refractory product manufacturers, in an attempt to withstand competitive pressure from outside Europe (especially China) in this sector and, especially, for standard ladle materials.

In fact, as they are derived from refractory materials for heavy-duty uses (basically, converter and electric furnace liners) they are made up of very pure magnesia, usually electro-fused, with a high graphite content, which produces a step up in terms of quality compared with standard magnesias, which are often used for ladles, providing a significant economic advantage in terms of content costs.

As a result, they are widely used in products for lining ladles, the sides of which can include products that contain 50%, 70% and even nearly 100% of the basic raw material.
The use of secondary raw materials

Recycled magnesia

![Image of recycled magnesia]

**DER MG90 R**
calcined magnesite

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO % 92</td>
<td>Water content % maxi 1</td>
</tr>
<tr>
<td>MgO % min 88</td>
<td>Density g/cm³ 2.9</td>
</tr>
<tr>
<td>Al₂O₃ % 0 - 2</td>
<td>Product without carbon</td>
</tr>
<tr>
<td>SiO₂ % 0 - 4</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ % 0 - 2</td>
<td></td>
</tr>
</tbody>
</table>

**Grades**
- 0/1/2/6 mm - 0/2/10 mm
- Other grain size available for

**Packaging**
- Big bag 1500 kg with pallet
The use of secondary raw materials

Recycled magnesia

Basically derived from safety systems for steel mills (EAF, SIV, COV) as well as from non ferrous industries, this recycled raw material is chosen for use in basic monoliths, especially:

- Castables
- Rammings and patchings
- Gunnings
- Dry masses for tundishes
- Wet gunnings for tundishes

The usage percentages vary from limited quotas in castings due to the absorption of water, to almost 100% content for gunnings.
The use of secondary raw materials

Electro-fused alumina zirconium silica

<table>
<thead>
<tr>
<th>Chemical properties</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ZrO₂</strong> %</td>
<td><strong>Water content</strong> % max</td>
</tr>
<tr>
<td><strong>Al₂O₃</strong> %</td>
<td><strong>Density</strong> g/cm³</td>
</tr>
<tr>
<td><strong>SiC</strong> %</td>
<td>1</td>
</tr>
<tr>
<td><strong>H₂O</strong> %</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Fe₂O₃</strong> %</td>
<td>2</td>
</tr>
<tr>
<td><strong>Grades</strong></td>
<td><strong>Packaging</strong></td>
</tr>
<tr>
<td>0/1 - 1/8 - 3/16 mm, 5/25 mm</td>
<td>Big bag 1500 kg with pallet</td>
</tr>
</tbody>
</table>

Other grain size available for composite concretes.
The use of secondary raw materials

Electro-fused alumina zirconium

This recycled raw material has gained in strategic importance for formulating refractory items for the steel mill and other industries (especially glass making), to the extent that it is becoming more than sufficient to meet the demand and create tension in the market.

Of the main uses, it is worth mentioning:
- Monolithic items for steel mills
- Monolithic items for cement factories
- Monolithic and shaped items for the glass industry
- Raw materials for ceramics items
- Melting aid for producing electro-fused items.

The percentage obviously varies according to use and availability but, in specific cases, it can reach values of 70% or higher.
The use of secondary raw materials

Other raw materials

Finally, there is a whole host of recycled raw materials not covered here for reasons of briefness, but that are important for specific niche markets and manufacturing, and that sometimes, despite limited quantities being available, may have significant technical - economic importance. Among these, we can mention:

- Silicon carbides
- Carbon
- Electro-fused spinels
- Magnesite spinels
- Magnesite - zirconium
- Chrome corundum slag
- Magnesium chromite
- Zircon oxide and silicate
- Insulation materials
- Dolomite
- Isostatic chrome
- And more…
Thank You for Your attention!

Serena Fasolini - Michele Martino

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