Recycling of Residues from Metallurgical Industry with the Arc Furnace Technology – RecArc
Life-cycle management in metallurgy

The protection of natural resources and the environment has been one of the key objectives of European policy for years. Saving primary raw materials plays an important role. Since the amount of these naturally occurring materials is limited, but the demand for them in a modern society is increasing, they must additionally be recovered from relevant waste and scrap products and residues as so-called “anthropogenic raw materials”.

The steel industry has had a pioneering role in the reuse of old materials, since it has covered a large part of its need for iron by the use of scrap metal for a considerable time. However, a number of other metals are necessary in the production of stainless, high-alloyed special steel without which our current life cannot be considered. In particular chromium is of great importance in its metallic form as an alloying constituent. Although high-grade steel scrap iron can be used as a raw material, scrap iron generation is too small to cover the high, continuously rising requirements for special steel. For this reason primary raw materials must increasingly be used. 7 million tonnes per year of high-grade steel are produced alone in Europe.

The situation

High-grade steel is produced in a melting metallurgical process. As is the case of every other steel types, a mineral molten material is also produced which floats on top of the melting bath due to its low density. All usually oxidic residual substances that cannot be combined with steel are enriched in this so-called "slag".

Certain alloying components of the high-grade steel, which react with the injected oxygen during the treatment of the melting bath, also belong here and get into the mineral melt in the form of oxides. Chromium, which can make up 4 % of the slag as chromium oxide, is particularly affected. In addition, fine steel droplets get into the slag due to the high turbulence during the melting process. Depending on the composition of the high-grade steel they also contain chromium but in a metallic form. Due to the two processes, important components of high-grade steel and the high-grade steel itself are present in the steel slag which impairs the product yield.

Composition of a high-grade steel slag.

Dicalcium silicate, a mineral formed from the chemical compounds lime and silicon dioxide, with an approx. 90% of the total mass is the main component of high-grade steel slag. Belite is a form of dicalcium silicate which is one of the most important components of the so-called "cement clinker". They are nut-sized, grey-green, stone-hard objects, produced in cement grinding. High-grade steel slag is inclined to physical decay during its cooling. Dicalcium silicate takes up a form which...
does not exhibit the binding behaviour necessary in cement. Despite its suitable chemical composition it cannot therefore be used in the cement industry. It can only be used in qualitatively low-grade areas of the construction industry, for instance as mine backfill. The chromium content of high-grade steel slags makes their use more difficult, since it is strictly restricted in many applications. If no suitable applications are available, or an low-grade use is associated with extra costs, the slags are landfilled. Thus the waste of natural resources is also accompanied with the loss of valuable void space. Two million tonnes per year of high-grade steel slag are produced in Europe.

Motivation

The constantly rising demand for high-grade steel leads to an increased need for metallic chromium. Therefore recovery from the slag, on whose practical properties the chromium does not have any positive effect, is aimed for. A part of the metallic components – high-grade steel droplets contained in the slag – can be separated and recovered using mechanical processing methods. However, the effectiveness of these methods is often low. Chromium, chemically bound as chromium oxide, cannot be recovered by mechanical methods at all. It is firmly combined in the slag phase and does not differ from this in its physical characteristics. Besides, the often insufficient quality of the slag due to its tendency to decay cannot be improved by mechanical treatments.

Objectives

The overall objective of the RECARC demonstration project supported by the European Union within the LIFE program is the recycling of all components of such high-grade steel slags. It includes

- complete recovery of all chromium-containing valuable materials as a metallic alloy and
- the upgrading of mineral slags to high-quality building materials.

By melting the slags under so-called "reducing conditions" the chromium compounds are converted to elementary, metallic chromium, which, together with the metallic components, separates as a metal alloy from the slag melt. This particularly chrome-rich alloy can then be used in place of primary raw materials for the production of high-grade steel. Simultaneously, using suitable additives and critical cooling conditions the melted slag strongly depleted in heavy metals is converted into a hydraulically active phase similar to typical cement components. This enables its use in the cement industry where slags from pig iron production – so-called blast furnace slags – have already been extensively used.

The project

Treatment of the high-grade steel slag by melting was performed in a semi-pilot closed arc furnace, similar to industrial-scale plant used in
the metallurgical industry for decades. Within the project the optimum operating parameters were determined under which an effective recovery and/or depletion of the chromium is possible. Numerous investigations on the efficacy of different additives were carried out which served both the depletion and separation of the chromium and influenced the quality of the treated slags. It was shown that an aggressive cooling enabled a clear-cut quality improvement of the slags. Model calculations were also carried out. Altogether more than 5 tonnes of high-grade steel slag were converted. It was estimated that to complete the work approximately 700,000 € was required, of which 50% was contributed as a support by the LIFE program of the European Union. The project took 3 years to complete and was carried out by Federal Institute for Materials Research and Testing – BAM (Berlin) together with the FEhS – Institute for Building Material Research e.V. (Duisburg).

The method

In the electrical arc furnace energy is transferred to the material to be melted – in this case high-grade steel slag – by graphite electrodes. It is converted into heat energy whereby the material heats up and finally melts.

If the slag is melted, the heavy liquid metal fractions sink to the bottom of the melt bath. There they agglomerate into a metal phase, on which the lighter mineral slag floats, still containing chromium compounds. In order to separate these chromium fractions bound in a mineral form, they must first be converted into the metallic form of chromium. This can be done by reducing agents, substances such as carbon, aluminium or silicon, which react with oxygen and are able to liberate chromium from its compounds. In the electrical arc furnace, carbon is set free at the graphite electrodes which penetrate into the molten material if the electrodes are close enough to the melting bath or even dip into the molten material. The carbon emitted by the electrodes is in itself a reducing agent. The quantity is however so small that only a part of the bound chromium is reduced to metal. Therefore additional reducing agents have to be added. As soon as the chromium compounds are reduced to elementary metallic chromium by these substances, they separate in a similar manner to the remainder of the metal and change into the metal phase. Reduction and metal separation take place simultaneously.

**RecAP**

When both processes have been completed, the composition of the slag with low metal content can be optimised regarding its intended purpose and then it can be cast.

**Reduction of the chromium compounds**

Highest priority was attributed to the recovery of chromium as a metallic alloy both contained in the metallic fractions and bound in mineral form. There were two reasons:

- a high-quality utilization of the slags is not possible even with characteristics otherwise appearing suitable, as long as the chromium content exceeds the permissible limiting values for the respective application. The slag is only available for a multi-purpose use when the chromium content has been considerably reduced. 0.2% chromium is currently considered as the limiting value for the use in cement.
The chromium-rich metal phase determines the economy of the method to a large extent due to its high value. The higher the yield of the chromium contained in the slag, the more worthwhile the treatment becomes from an economic aspect.

The effectiveness of the reduction of chromium bound in mineral form greatly depends on the process parameters at which the arc furnace is operated. As a result of systematic tests it was found that an appropriate chromium depletion – from about 3% to a maximum of 0.2% – is only possible when the graphite electrodes dip directly into the molten material. In this so-called "operation in resistance" energy is transferred directly through the immersed electrode surface and not via an arc. In addition, petrol coke – a light, porous form of carbon – has to be added as an additional reducing agent. Chromium content of 0.1% or less obtained under these optimum conditions is even less than the desired limiting value of 0.2% for cement. In addition to the high effectiveness – over 97% of the chromium contained in the slag is recovered – the slag can be used more extensively without any further optimisation.

Chromium content after thermochemical treatment as a function of the reducing agents used. An untreated slag is also represented for comparison.

Optimisation of slag quality

If the slag is only to be used as a material for road construction, it is usually sufficient to cast it in molds and leave it to cool at air temperature after completion of the reduction and metal separation. A rock-like mass is formed, whose properties are not low-grade to those of natural mineral materials and can replace them due to their low chromium content.

However, if the slag is intended to be used as a raw material in the cement industry, it is reasonable to optimise its chemical composition by adding quartz sand (silicon dioxide, SiO₂) or alumina (aluminium oxide, Al₂O₃) before casting. It is necessary for example that the majority of the slag solidifies into a glasslike material, since only glassy slags exhibit the hydraulic setting behaviour necessary for cement. For this purpose the slag must contain a certain amount of the chemical compound SiO₂. If the content is too low, quartz sand is added to the molten material. The addition to the molten material has the crucial advantage that the quartz sand is immediately dissolved and integrated in the slag phase.

In order to achieve a glasslike solidification of the molten materials, cooling must take place very rapidly. For this purpose the slag was "granulated", a method in which the liquid slag jet is directed through a special device where it is swirled with air, water or both and thus cools extremely fast to ambient temperature. Such a treatment produces a granulated slag of pinhead-size, glassy slag fragments whose content of glassy solidified phases is 99%. Thus it is perfectly suited for use as a raw material in the cement industry.
The products

The thermochemical treatment performed in RecArc converts the high-grade steel slag into two products: a chromium-rich metal phase and a mineral phase. With constantly rising raw material prices the metal phase with a chromium content of approx. 50% is of high value for the production of such steels that contain chromium as an alloying constituent. Since in addition to chromium the metal phase only contains metals or elements that are components of most steels – iron, manganese, vanadium, nickel, carbon and silicon – no subsequent processing is needed: it can be used directly as a raw material. Chromium, which would be lost with low-grade use or through landfilling of the untreated high-grade steel slag, is thus returned into the material cycle.

Separated chromium-rich metal phase after "reducing melting treatment" of a high-grade steel slag in the electrical arc furnace.

High-grade steel slag with low chromium content after thermochemical treatment in the arc furnace, left as lumpy slag which is suitable for road construction, right as slag granulates which can be used as a raw material component in cement.

The second product, which constitutes over 90% of the total mass, is the mineral phase. The results of the project showed that a suitable process can upgrade the untreated high-grade steel slag which is only suitable for a low-grade use, to a mineral material with a multi-purpose use in the construction industry. Its fields of application are chiefly determined by the treatment of the molten material: if the slag is cast in molds where it can solidify in a crystalline way, a lumpy mixture of mineral materials is obtained which can be used in road and railway construction after a mechanical crushing. However, the addition of suitable additives to the liquid slag and their granulation can provide a raw material with a hydraulic setting behaviour suitable for the cement industry. Thus the potential of the slag based on its raw material components can entirely be exploited.

Benefit to the environment

But what is the benefit of thermochemical treatment of the high-grade steel slag to the environment?

The recovered metal phase could replace some of the primary raw materials which are needed for the production of high-grade steel. Nevertheless a thermochemical treatment can produce about 40 kg of chromium from 1 tonne of slag. This amount is sufficient for the production of 300 to 400 kg of high-grade steel. Converting these values to the estimated quantity of high-grade steel slag in Europe, it is 80,000 tons of chromium or 600,000 to 800,000 tons of high-grade steel! For a comparable quantity of chromium metal from natural ore resources far more than 700,000 tons of overburden must be moved. The recovery is therefore entirely within the substance of the Life-cycle Management Act – the minimization of the exploitation of natural resources for a product. Thus not only the
limited resources of primary raw materials are saved over the long term, but large areas of nature are also preserved which would have been irreversibly damaged by mineral extraction.

Limestone extraction in a quarry for cement production. Primary raw material extraction always represents an intrusion in nature and the environment. The need for natural primary raw materials could be reduced by using treated high-grade steel slag in cement.

The same applies to the mineral slag which constitutes the vast majority of the high-grade steel slag: because of the suitability of the treated slag as raw material for cement, a portion of natural raw materials otherwise used can be replaced which are usually extracted from large open-pit mines. Thus substantial natural resources can be saved and the necessary surfaces for raw material extraction be minimized.

One disadvantage of the method is the relatively high power consumption in the electrical arc furnace. However, the energy consumption is put into perspective if one considers that smelting the mined chromium ores, which provides the chromium as a usable metal in the first place, is based on the same principles as chromium recovery using the RECARC method and therefore requires an equivalent high energy input. The high energy consumption must also be considered in the production of cement raw materials from natural materials such as lime, clay and others. Only “burning” of these raw materials at temperatures up to 1500°C produces the so-called “clinker phases” which constitute the main part of the cements whereas these phases are already present in the treated high-grade steel slag. In addition, large quantities of the greenhouse gas CO₂ are set free during cement production from natural raw materials, additionally to the CO₂ emission which results during production of the necessary energy. Over 400 kg CO₂ are produced by the thermal treatment of a tonne of lime – that are over 20,000 litres of the greenhouse gas. With an approximate quantity of 30 million tonnes of limestone per year used for cement production alone in Germany, this is 12 million tonnes of CO₂. If a part of the raw materials is replaced by the treated high-grade steel slag, the emission of approx. 400,000 tons of CO₂ could be avoided. Thus in addition to shutting material cycles, which often necessitate polluting individual solutions, a contribution to reducing the CO₂ emission would also be made.

Conclusions and outlook

The European Union LIFE project RECARC has demonstrated that unused or low-gradely used resources contained in high-grade steel slags can be completely recuperated or re-used by a treatment in the electrical arc furnace. This thermochemical treatment using a "reducing melting" enables the enrichment of chromium-containing valuable materials from the slag in a metal alloy thus cleanly separating them from the mineral slag components. Extensive tests have shown that a suitable process can ensure the recovery of these valuable materials in excess of 97 %. It has also been proved that suitable additives and a granulation can upgrade the mineral component of the slag to a material whose composition and properties correspond to those of typical cement components.

Granulated blast-furnace slag – a granulated slag from pig iron production – is already often used for more environmentally friendly cement production. RECARC demonstrates that high-grade steel slag can also be used after a thermochemical treatment under reducing conditions as an additive in cement.
The material is granulated: it can then be used directly as a raw material for cement production. But first, the legal conditions must be established, since the raw material is subject to strict conditions and the cements must meet certain standards.

The possibility of recycling demonstrated by RecArc enables material cycles to be established which would otherwise lead to a loss of valuable raw materials. Since the arc furnace technology has been used in the metallurgy industry for decades, the infrastructure necessary is available, thus the industrial application of the method is fairly simple. In addition, the small-scale technical demonstration guarantees good transferability of the results to an industrial scale. To begin with rising raw material costs but later on, the increasingly stringent limits for CO₂ emission make handling metallurgical residues highly relevant. Transfer to industry of the method demonstrated in RecArc could make an important contribution to a sustainable saving of natural resources and the environment.

The quality of high-grade steel slag will be improved by thermochemical treatment in an arc furnace, so that it can be used for many applications.

While the recovered chromium-rich metal alloy is a suitable metallurgical raw material for the production of high-grade steel, the slag can be used after the treatment due to its low chromium content (less than 0.1%) in the construction industry for many purposes. The highest increase in value is reached when the slag composition is optimised and the material is granulated: it can then be used directly as a raw material for cement production. But first, the legal conditions must be established, since the raw material is subject to strict conditions and the cements must meet certain standards.

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Further information:
http://www.recarc.bam.de