14

# Possible Uses of Steelmaking Slag in Agriculture: An Overview

Teresa Annunziata Branca and Valentina Colla
*Scuola Superiore Sant'Anna - PERCRO - TeCIP Institute*
*Italy*

## 1. Introduction

Slags are the main by-products generated during iron and crude steel production and the steel industry is committed to increasing and improving their recycling.

Over the past decades, the steel production has increased and, consequently, the higher volumes of by-products and residues generated have driven to the reuse of these materials in an increasingly efficient way. In recent years new technologies have been expanded, and some of them are still under developing, in order to improve the recovery rates of slags. On this subject material separation technologies and carbon sequestration could dramatically reduce $CO_2$ emissions from steelmaking processes. On the other hand, the increase of slags recovery and use in different fields of application, such as in agriculture, allowed to reduce landfill slags and to preserve natural resources. In addition to the environmental achievements, these practices produced economic benefits, by providing sustainable solutions that can allow the steel industry to achieve its ambitious target of "zero-waste" in the incoming years (worldsteel, 2008).

Steel is produced by mean two main ways:

1. the iron ore based steelmaking (Fig. 1), which represents about 60-70% of the world steel production. The main raw materials are: iron ore, coal, limestone and recycled steel scrap. The main production routes are: the ironmaking iron ore based on Blast Furnace (BF) followed by steelmaking in the Basic Oxygen Furnace (BOF), and the ironmaking based on Direct Reduction of Iron ore (DRI), followed by steelmaking in the Electric Arc Furnace (EAF). In the BF coke is the reducing agent of iron ore. Limestone or dolomite (fluxes) are added into the blast furnace where they react with iron ore impurities, such as silica. Steel is produced from pig iron, scrap and lime in the BOF, where oxygen is blown to burn off the carbon.
2. the scrap-based steelmaking (Fig. 2), which represents about 30% of the world steel production. This way is based on the scrap recycling in the EAF, where the main input are steel scrap and electrical energy that is needed to melt the scrap into steel.

In both BOF and EAF the reactions between oxygen, carbon (carbon as gaseous carbon monoxide), silicon, manganese, phosphorus and some iron as liquid oxides produce oxidized compounds that react with lime or dolomitic lime to form slag. At the end of the refining operation, after steel pouring into a ladle, the slag is poured into a vessel and is subsequently tapped into a slag pot.

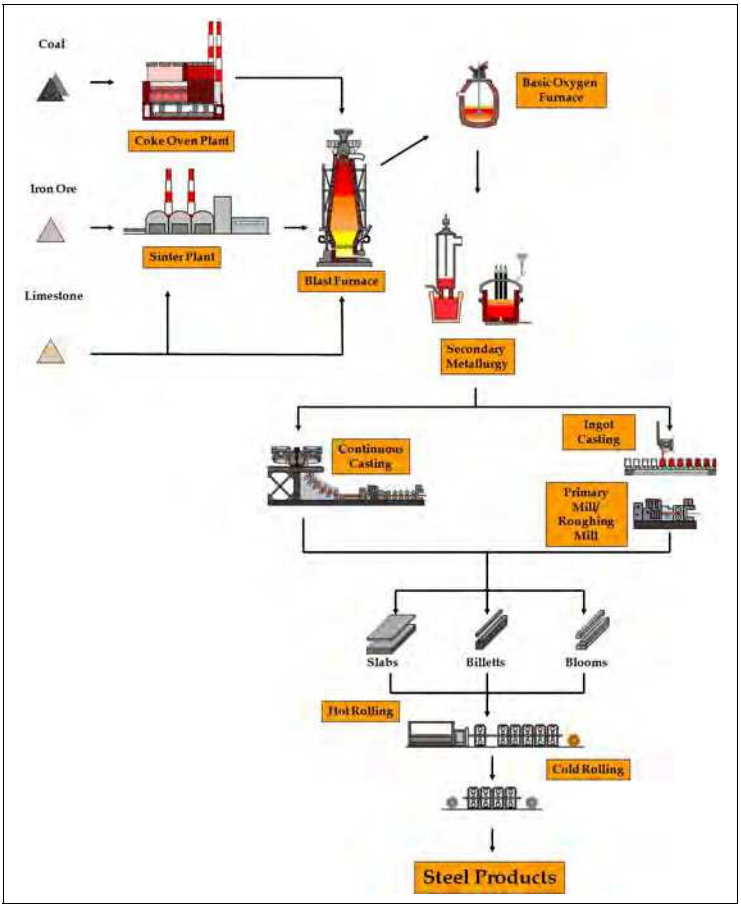



Fig. 1. The iron ore based steelmaking.

The main by-products resulting by ironmaking and steelmaking are slags (that represent 90% of the total by-products), dusts and sludges. On the average about 200 kg of by-products per ton of steel result from the steel production through electric arc furnace, while about 400 kg of by-products per ton of steel production through BF/BOF (World Steel Association, n.d.).

The use of by-products from steel industry goes back to many centuries ago. In 350 BC Aristotle already stated "When iron is purified by fire, there forms a stone known as iron slag. It is wonderfully effective in drying out wounds and results in other benefits". In later centuries slag has been used as construction material. The discovery of the hydraulic properties of granulated BF slag gave birth to a new era in slag exploitation: slag has been used as binding agent and/or addition for concrete. The use of steelmaking slag, from Basic-

Bessemer or Thomas processes, as phosphating and/or liming agent started in 1880 (Geiseler, 1996).

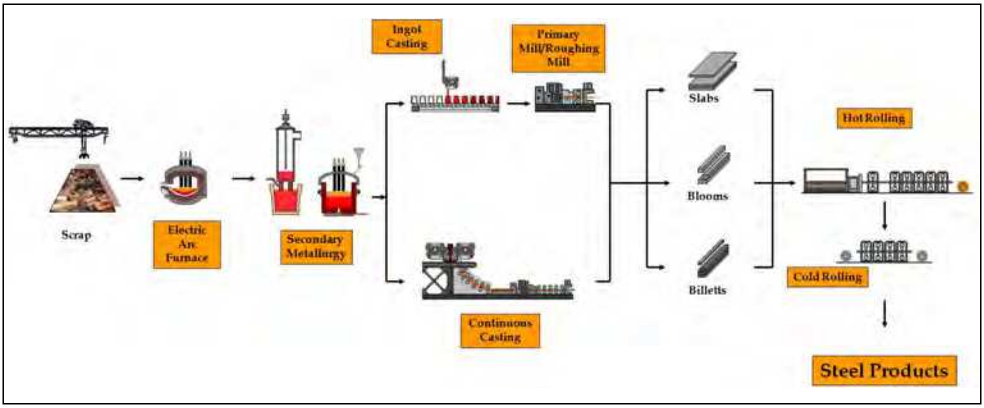



Fig. 2. The scrap-based steelmaking.

The traditional use of slag as landfill material, after the increase of steel production since the mid-1970's, has reached its limit and the pressure for natural resources and energy saving have driven steel industry to increase the recycling of this material, by facing other important challenges (such as technologies development, production facilities maintenance and ferrous slag products certification) in order to improve their application in different sectors (The Japan Iron and Steel Federation – Nippon Slag Association, 2006).

Slags coming from both BF and steelmaking processes are consumed at steelworks, used in cement, roadbed material, ground improvement material, civil engineering material and fertiliser. Once slags were dumped; nowadays they are considered marketable products and only a small percentage is processed as industrial waste in landfills.

In the past steelmaking processes were exclusively designed for the production of specific quality of iron and steel. One of the current steelmakers' goal is to design processes to produce high quality slags, both prior to and during the slags production, according to the market requirements, in order to satisfy environmental and technical requirements of international and national standards (Euroslag, 2006). On one hand, selling by-products produces revenues for steelmakers, that in turn generate economic development for the worldwide industry. On the other hand, the sustainable use of slags contributes to natural resources saving, to $CO_2$ emissions reduction, to energy consumption reduction, to the formation of a society founded on the recycling practice (as landfilling is avoided) and to the promotion of the steel industry sustainability. Therefore potential economic and environmental benefits make slags by-products that can be further recovered and used. For all these reasons, the effective utilisation of slag turns it into high value added product and allows to improve competitiveness of the steel industry.

This chapter intends to review the state of the art related to the use in agriculture of steel slag, mainly coming from BOF process using basically Linz-Donawitz (LD) converter, in different worldwide contexts. The review covers different aspects by summarizing its use as fertiliser and as liming agent, its potential use as amending material for soils, and by paying attention also to different technologies and methodologies aiming to improve the quality of the slag, in order to increase and make progress in its use in agriculture. On one hand, studies based on the use of slag in agriculture will be considered, which treat the use of steel slags for amending acid soils and as source of important factors and growing agents (not only calcium and magnesium compounds, but also other elements such as silicon, providing important beneficial effects for some crops and increasing the plant yields) and its use as Fe source for reducing Fe chlorosis in different crops. Moreover, investigations will be described concerning the heavy metals contained into the slags and their behaviour on the soil, in order to evaluate possible harmful effects after slag application for agricultural purposes and to avoid their possible negative environmental impacts, as well as the use of steel slags for metal stabilisation in contaminated soils. On the other hand, investigations focused on the obtaining a slag with high phosphorus content to be used as fertiliser (together with other slags with a low content in phosphorus to be recycled inside the steelmaking process) will be discussed.

## 2. Ironmaking and steelmaking slags and their use

Every year more than 40 million tonnes of iron and steel slags are produced in Europe. The production of iron and steel slag in Europe in 2008 was of 45.6 million tonnes[1] and decreased in 2009 and 2010 only due to the steel production slow down caused by the economic crisis. The main compounds contained into the slags are calcium, silicon, magnesium, aluminium and iron oxides.

Slags are generated in all stages of steel production and the following four different kinds of slags from different routes can be identified: BF slag, BOF slag, EAF slag and Secondary Steelmaking Slag. The slagging agents with fluxes, such as limestone, dolomite and silica sand, are added into BF or steelmaking furnaces in order to remove impurities from ore, scrap and other ferrous charges during smelting. The slag formation is the result of a complex series of physical and chemical reactions between the non-metallic charge (lime, dolomite, fluxes), the energy sources (coke, oxygen, etc.) and refractory bricks. Because of the high temperatures (about 1500°C) during their generation, slags do not contain any organic substances. The slags protect the metal bath from oxygen and maintain temperature through a kind of lid formation. Due to the fact that slags are lighter than the liquid metal, they float and may be easily removed. Slag is generated in a parallel route of the main processes of hot metal production in ironmaking and steelmaking and therefore the slag generation process is considered as a part of the whole steel production process (EC, 2001).

The uses of different types of slags in Europe are shown in Figure 3. Ironmaking and steelmaking slags are used in different ways with high added value. While steelmaking slags are mainly used for road construction, hydraulic engineering, and fertilizer, BF slag is mainly used for cement production[2].

[1] Source: European Slag Association, EUROSLAG
[2] Source: European Slag Association, EUROSLAG

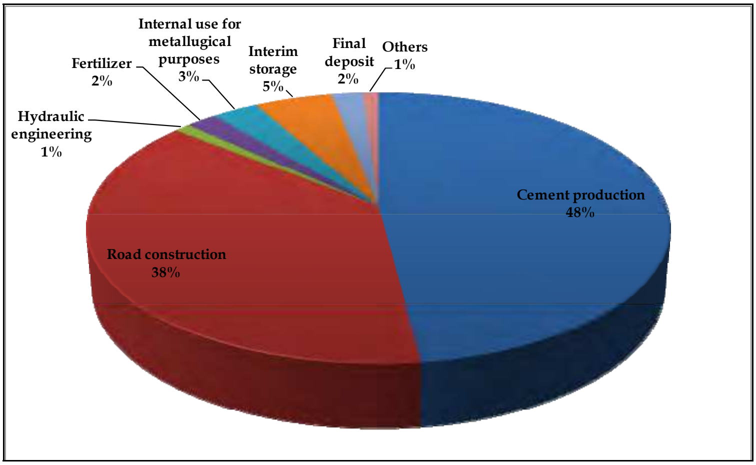



Fig. 3. The uses of different types of slags in Europe.

The marketed BF slag can be subdivided into three main types, depending how they are cooled:

- The Granulated BF Slag (GBFS) is produced by injecting high pressure water, followed by quenching and granulating it. It is used as material in cement, as fine aggregate for concrete and in civil engineering works, exhibiting better long-term strength, better resistance to chemical attack, and it brings down the cost of cement.
- The Air-cooled BF Slag (ABFS) is discharged to a cooling yard and naturally cooled with moderate sprinkling. The crystallized slag, after crushing, sieving and removing magnetic matter, can be used as construction aggregate, concrete products, road bases and surface and clinker raw material.
- The third type of cooled BF slag is represented by Pelletised Slag, with a vesicular texture, used as a lightweight aggregate and, when it is fine grounded, as cementitious material.

Steelmaking slags include slags from BOF and EAF. Since at this stage the steel production processes vary, depending on the steel being made, the slags chemical properties change as well. This results in a more difficult use of steel slags compared to the BF slag. They are discharged to a cooling yard or to a slag ladle and they are naturally cooled with moderate sprinkling. After crushing, sieving and removal of magnetic matter, they achieve granularity appropriate to different applications. Because of their lime contents they expand in reaction with water. After this expansion they are stabilised by “natural ageing” for long periods outdoors in natural rainfall and other weather or “steam ageing”, through high-temperature vapour.

Steelmaking slag deriving from BOF process (using the Linz-Donawitz (LD) converter) comes from the pig iron refining process, which converts molten pig iron and steel scraps into high quality steel. Most slags from steel plant derive from this process, with an average of 150-200 kg of slag generated per tonne of steel produced. X-ray diffraction studies have shown that the major phases present in LD slag are dicalcium ferrite, calcium alluminate and wüstite, but it contains also some reactive mineral phases, such as $2CaO{\cdot}SiO_2$, $3CaO{\cdot}SiO_2$ and free CaO e MgO (Das et al., 2007).

The EAF slag utilisation is quite similar to the one of BOF slag, but, due to its lower lime content, EAF slag is very stable and can be used in asphalt without any problems.

Secondary Steelmaking Slag disintegrates into a powder due to instability of the dicalcium silicate, causing an increase in dust emissions to the environment. Some studies have successfully been carried out in order to reduce this phenomenon and to make this slag suitable for use and valuable (Rozman et al., 2007), (Branca et al., 2009).

Recently, due to a better understanding of the slag formation mechanisms and of the overall BF process, a large number of different slags has been designed, and it is also currently possible to control, optimise and minimise slags production. This progress applies also to BOF slag. The silicon, phosphorous and sulphur removal, before the refining into the basic oxygen furnace, has led to the reduction of tap-to-tap time, to the costs decrease, to the reduction of the amount of slag produced and to the production of higher quality steels. Moreover, through the vacuum degassing process, after decarburisation in the BOF, the hydrogen and nitrogen contents have been reduced. The ladle treatments produced significant reduction in impurities in steel and the use of selected slags minimised the formation and modification of *inclusions* (usually they are non-metallic particles contained in steel, that, depending on their number, their size and their distribution, can have a detrimental effect to mechanical properties of steel), with the result of improving mechanical properties of steel (Dippenaar, 2004).

Some slags are internally used in steelmaking furnaces or in sinter plants, while about 50% of this kind of slag is used outside the plant in the construction sector, mainly for road construction, as an aggregate in bituminous pavements, as a binding agent in base courses, for strengthening the subsoil and for soil conditioning. Free lime, after separation, can be used as fertiliser, in cement and concrete production, for waste water treatment and in coastal marine blocks. In soil conditioning slags are efficient in soil neutralisation. In addition, the siliceous liming materials improve soil structure and reduce fungal infections. Blast furnace slag can be used also in agriculture because of its high sorption capacity of phosphorus, which remains into the available form for the plants. Negative effects, resulting from steel slags use, could derive from their heavy metal concentrations, but such metals tend to bound to the slag matrix and thus they are not available for plants. All these factors contribute to underline positive effects of using slag as liming materials, that lead to better yield of the crops, soil protection and reduction of natural resources consumption (R. Hiltunen & A. Hiltunen, 2004).

### 2.1 The main legislation about the use of slags

Over the past decades the by-products recovery and reuse have significantly increased also because of the stringent legislation for environmental protection, that differs all over the world. In Europe, slag is mainly bound to the Waste Framework Directive (WFD), but the main legislation concerning the use of slag includes other laws, as follows: the Kyoto protocol, the Reference Document of Best Available Techniques, Harmonisation Committees TC 351 Dangerous Substances and TC 154 Aggregates, the REACH directive.

The main issue concerning the use of ferrous slags is the question whether it is a waste or a by-product. In order to market them the better way is to consider them by-products because the term “waste” indicates a material to be deposited instead to be used (Kobesen, 2009).

The Waste Framework Directive (WFD) (2006/12/EC) is the most important document governing the use of slag. Until recently, slag was considered as waste, but, after many years of discussion, the WFD has been amended by adding the term by-product (2008/98/EC). On one hand, the WFD provides the main concepts and definitions concerning the waste management; on the other hand, it sets the principles of waste management. Moreover it clarifies the definition of waste by introducing definitions of by-product and *end-of-waste* status, thanks also to the work of steel industry in supporting the EU Commission. The most important articles for the slag use are, as follows:

- Article 3, which provides the definition of waste and hazardous waste;
- Article 4, which describes in what order wastes are to be discarded;
- Article 5, which concerns by-products and provides the following conditions to meet in order a by-product is not considered a waste: direct use of a by-product, without any further processing other than normal industrial practice; by-product production as an integral part of a production process; any further use has to be lawful and certain; the by-product use has to be consistent to the principles of the EU waste policy, such as environment and human health protection.
- Article 6, End-of-waste status, regulates when a substance is classified as waste, ceases to be waste. The article 6 of the WFD defines the end-of-waste (EOW) criteria and what requirements have to be met. These criteria are developed in accordance with the following four conditions:
    1. The substance or object is commonly used for specific purposes
    2. A market or demand exists
    3. The substance or object fulfils the technical requirements and meets the existing legislation and standards
    4. The use of the substance or object will not lead to overall adverse environmental or human health impact.

The EOW criteria shall embrace limit values for pollutants where necessary and shall take into account the possible adverse environmental effects of the substance or object (Eloneva et al., 2010).

The Kyoto Protocol (Conference of the Parties, 1997), drawn in 1997 and come into force since 2005, regulates and decreases $CO_2$ emissions down to the 1990 $CO_2$ emission levels, because of its key role in the global warming.

The use of slag in different fields of application, for example the granulated BF slag (GBFS) as substitute for cement and for clinker in cement and the steelmaking slag for soil conditioning, can allow the reduction of the tonnages of $CO_2$ emission. Furthermore, in order to reduce the $CO_2$ emissions from the ironmaking and steelmaking processes, some studies have been carried out to sequestrate $CO_2$ in slag, through the free lime (CaO) and the di- and tricalciumsilicates carbonation (Abassapour et al., 2004).

The BREF document (EC, 2001) provides the best available techniques concerning environment, health and safety for iron and steel industry. It has been recently revised (EC,

2009) and, among other things, it gives the guidelines for EU Member States about the best available techniques for producing, treating, processing and using slag.

The new European Regulation No 1907/2006 for Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), adopted by the European Parliament and the European Council in December 2006, came into force on 1st June, 2007 (EC, 2006). This is not a directive, but a regulation, which replaces some national regulations and directives with a single system. It aims at: providing a high level of human health and environmental protection; ensuring that people are responsible to understand and manage the risks linked with the use of chemical substances that they put on the market; consolidating innovation and competitiveness of the EU chemical industry; encouraging the implementation of alternative methods for evaluating of the hazards of substances; promoting a free circulation of substances on the internal market while enhancing competitiveness and innovation (Kobesen, 2010). The registration concerns only products or by-products, while wastes are excluded from registration obligation. The regulation comprises new substances (substances which are put on the market after 18th September 1981) and phase-in-substances (substances which have been put on the market before 18th September 1981). Phase-in-substances are already registered in the so-called EINECS register (European Inventory of Existing Commercial Chemical Substances), whereas new substances will be registered in the ELINCS register (European List of Notified Chemical Substances).

Since the steel industry has been committed to clarify that iron and steel slag is produced and sold as by-product but not as waste, it was clear that ferrous slag had to be registered under REACH as a substance before 1 December 2010. In this respect the FEhS-Institute initiated the formation of a Consortium "Ferrous Slag", open to all European producers of iron and steel slag, in order to make a joint registration (Bialucha et al., 2011).

With regard to the Harmonisation Committees, the Technical Group (TG) 13, within the Technical Committee (TC) 154 concerning aggregates, deals with Dangerous Substances, by producing standards about release of some dangerous substances from aggregates. These include natural aggregates, ironmaking and steelmaking slags, defined of manufactured lightweight aggregates and recycled aggregate from material previously used in construction. The standards have to be compared with geologically similar deposits and Regulated Dangerous Substances (RDS) released are compared and identified. For slags the relevant RDS are, as follows: mineral oil, metals like V, Cr, Zn, Pb, Mo, As, Hg, Cd, other inorganic substances such as chlorides and sulphates (Kobesen, 2009).

Member states used different methods of investigation, which have to be harmonised. For example, the objectives of the Technical Committe 351 ("Construction Products – Assessment of release of dangerous substances") WG 1 are to:

- enable product TC to select the appropriate test;
- determine the release performance;
- ensure methods are scientifically sound;
- be relevant to CE marking of the product.

The following three technical specifications have been proposed (Bialucha et al., 2011):

1. TS-1, describing principles for selecting appropriate leaching tests for a specific product;

2. TS-2, describing a dynamic surface leaching test (DSLT);
3. TS-3, containing information on horizontal up-flow percolation test.

## 3. The use of converter slag

LD slag can be used in different fields of application such as fertilizer, soil conditioners, recovery of metal values. Because of its hard characteristics it is also used as aggregates for road construction, for the base and sub-base layer in road construction and for hydraulic engineering structures. On this subject tests have been carried out in order to assess technical properties. In particular the volume stability, which is the key aspect for using steel slags as a construction material, has been evaluated, by comparing the behaviour of slag under practical conditions, such as in road constructions; on the other hand, the assessment of environmental compatibility of aggregates as building material has been tested through leaching tests in order to continuously control quality (Motz & Geiseler, 2001).

Since 1880 steelmaking slag from Basic-Bessemer or Thomas process has been used as a phosphatic fertiliser, but also the current LD slag composition (mainly containing CaO, MgO, $SiO_2$, Mn and other valuable micronutrients, such as copper, zinc, boron and cobalt) makes it suitable as liming materials. On one hand, calcium and magnesium compounds, because of their basicity, improve soil pH; on the other hand, they are also plant nutrients and stabilisers for soil aggregates. Physical treatments of slag as well as its mineral composition influence the solubility and plant availability of the nutrients.

Silicate has a special bond in the slag minerals and it is useful for plant nutrition and soil quality. In fact silicate provides beneficial effects on plant health and soil structure, increase the phosphate mobility in the soil and the efficiency of phosphate fertilisation (Rex, 2002).

### 3.1 The use of steelmaking slags as fertilisers and as liming agents

Although the by-products recycling has always been a commitment of the steel industry, the growth of steel production in recent years has pressed the sector for increasing their use in a more effective way, in order to achieve a sustainable steel production. Even though steelmaking slags are continuously studied in order to improve their recycling, there are some limiting factors for their use. In particular a small amount of slags is used as fertiliser in agriculture and this use depends on the market situations. Due to the low market value of fertilisers, the long distances transportation is a limiting factor. In addition natural lime stone fertilisers are in competition to the slag use. Therefore the development of new markets for the slag, in order to ensure its utilisation in the future, is required. In this respect the steel industry is committed to minimize the amount of slag which has to be deposited, by improving its use through the increase of its properties (Drissen et al., 200).

Until the eighties steel was produced via the Thomas-Bessemer process, through the open hearth furnaces. The resulting slag containing phosphate has been used as fertiliser for about 70 years. The current steelmaking process is based on the Basic Oxygen Steelmaking process, where a basic slag is produced in the Linz-Donawitz converter. The LD slag contains about 1-3 wt% of $P_2O_5$, which is too low to be used as phosphate fertilizer, but, at the same time, it is too high to be used in the BF or recycled in the sinter plants.

Nevertheless the LD slag contains high levels of lime (CaO) and MgO that make it a potential liming agent, may improve soil pH and can be used as plant nutrients. Particularly free lime, which is one the main slag constituents, can partially dissolve by reacting with water to produce calcium hydroxide, $Ca(OH)_2$, as shown in Eq. (1):

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

The calcium hydroxide dissolves into $Ca^{2+}$ and $OH^-$, resulting in a pH increase.

All these factors characterizing this material, can allow to recycle an industrial residue and to improve the fertility of acid soils.

On this subject some studies have been performed in several countries. Among these a three-years research carried out in the Basque Country of northern Spain, by using LD converter slag on pasture land, has produced significant results (Besga et al., 1996). The comparative study analyzed soil modifications produced by LD slag and those produced by traditional liming agents. In particular, the influence on soil pH, soil Ca and Mg content, the percentage of Al saturation and the yields have been taken into consideration in this study. The achieved results concern different aspects that have been considered in it. Firstly, increasing rates of LD slag application have increased the soil pH linearly, that, as a consequence, has led to Al solubility decrease; this has allowed the P absorption, due the changing of insoluble forms to soluble ones. In addition the Ca and Mg soil contents increase, resulting in an increased yield, while the consequence of the pH has reduced the toxic effects of Mn (e.g. on the white clover). On the other hand, the Cd, Cr and Ni monitoring has shown that, after LD slag application, there was not heavy metals accumulation in the soil.

A research project that was funded by the Research Fund for Coal and Steel (RFCS) programme (Kühn et al., 2006), led to relevant results about the liming and fertilising effects of fine grained iron and steel slags, such as BF slag, LD slag or ladle slag, compared to other liming materials, such as burnt lime or carbonate limestone, in field trials investigations as well as in greenhouse pot experiments. The research aimed to investigate the fertilising effects on both the soil and the plants. These investigations have been carried out in arable land (Germany, Austria and Spain), in green land meadows (Germany and Spain), and in forestry (Spain). Furthermore the behavior of trace elements, such as Ca, Mg, P, Cr, V, Zn and Pb, in soils and plants has been investigated, in particular, the behavior of heavy metals, especially of Cr and V, their mobility and their bonds in the soil.

Investigations carried out on soil and yield have proven that the yields of experimental crops, in long term experiments by using iron and steel slags, were higher than those achieved after using different liming materials; on the other hand, pH has increased in the same way as a result of the use of both kind of materials. The use of basic slag in soil tests has produced the same fertilising effects, while the results of P content and soil pH has been higher, compared with super phosphate or rock phosphate use.

The comparison between the converter slag and the converter sludge applications to soils and tea plants, conducted in northern Iran, produced effects on soil properties and on the tea plant nutrient concentrations (Jamali, S. F. K. et al., 2006). Results have shown that converter slag application increased soil pH more than converter sludge treatment, probably because of the higher original pH of the slag. In addition they have supplied Ca and Mg to soil and, consequently, their concentrations have increased in tea leaves.

The use of alkaline slag for amending acid soil and improving plant growth has been analysed in a recent study carried out in Iran (Ali & Shahram, 2007). After the application of increasing amount of slag, the soil pH proportionally increases. Moreover, at pH values between 7.4 and 8.5, the Fe availability decreases, while at higher pH values it increases; on the other hand, the P and Mn availability proportionally increases. The greenhouse studies have shown that the slag application (1% and 2% (w/w)) in tea garden soil and (0.5, 1 and 2%) in rice field soil leads to the increase of plant yield and the P and Mn uptake; an increase of Fe and K uptake has been detected in rice field, a decrease of K uptake in tea garden has been observed, while Fe uptake has not been changed.

The same results have been achieved after the application of basic slag in acid sulphate soils in an incubation study. The investigation aimed at assessing the ability of basic slag to neutralize acid and its effectiveness on the solubility of basic cations in the soils, in order to achieve a sustainable use of acid sulphate soils in coastal areas of Bangladesh (Shamim et al., 2008). A wide range of processes can lead to the addition of acid cations and the removal of basic ones in the soils. The acid water, penetrating into the ground, through the leaching process, tends to increase the acidification of the soil, except if bases are compensated by different sources, such as atmospheric deposition. When acid cations are in soil solution, they tend to replace basic cations. This can also affect the metals and metalloids mobility in the groundwater, with the result that this can be a threat to groundwater and the health of aquatic and terrestrial ecosystems. Incubation experiments showed that basic slag increases soil pH, mainly due to its neutralizing effect that releases basic elements in the acid sulphate solution. This process reaches the highest value after 180 days of incubation under saturated moisture condition, probably due to slow releasing of basic ions from basic slag. In addition the application of basic slag increases K, Ca and Mg in soils, although, in some cases, over the course of time, a small decrease of this trend has been observed, probably because of the formation of insoluble compounds of Ca and Mg.

### 3.2 Steelmaking slags as a silicon source for plant

After oxygen, silicon (Si) is the most abundant element in the earth's crust. Along with some other elements that are not considered essential, under particular agro-climatic conditions, it can increase the crop yields by promoting some physiological processes. Silicon sources for agricultural purposes must display some important features, such as high soluble Si content, low cost, availability for plants, balanced ratios and amounts of Ca and Mg, increase of phosphate mobility, suitable physical properties, easy application, and absence of heavy metals.

In order to have an effective use of Si fertilization in agronomic practices, an adequate knowledge of physical and chemical characteristics of Si sources and of the rates and methodologies for applying them are needed. A number of field and greenhouse studies have demonstrated that the use Si soil amendments increases crop production and quality. The application of Si fertiliser has beneficial effects on both rice and sugarcane. Although the mechanism of response of sugarcane to Si fertilization is not yet well understood, some studies have shown that the yield increase of the sugarcane may be associated with different factors, such as Al, Mn and Fe toxicity alleviation, increased P availability, reduced lodging, improved leaf and stalk erectness, freeze resistance and improvement in plant water economy. Furthermore the Si accumulation protects plants from certain diseases, such as a resistance to biotic and abiotic stresses (Savant et al., 1999). The use of Si in the plants can help the plants against pathogen attacks (Motz & Geiseler, 2001).

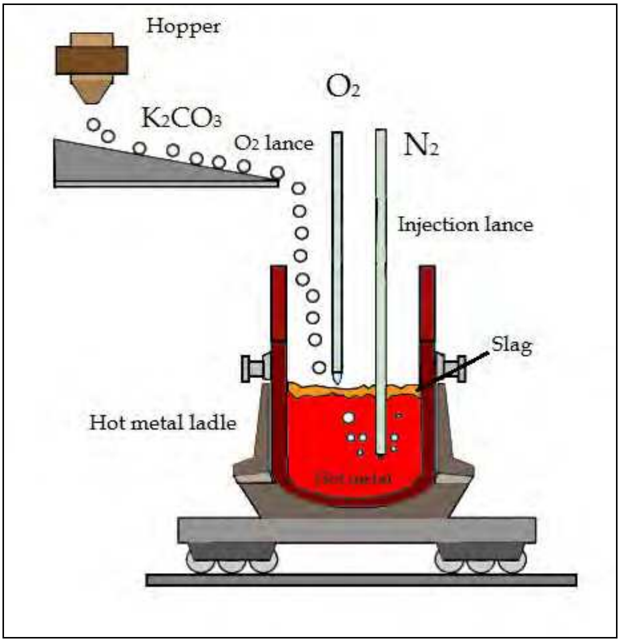



Fig. 4. Production of potassium silicate fertilizer from steelmaking slag (Takahashi, 2002).

The use of silica ($SiO_2$) as a fertiliser increases the rice resistance to diseases and vermin. For this purpose the slag produced in the hot metal desiliconization process, which contains mainly silica, has been taken into consideration in order to develop a potassium silicate fertiliser. This is an example of a new steelmaking process developed by NKK (Nippon Kokan Kabushiki Kaisha) and referred as ZSP (Zero Slag Process), focused on the reduction of the amount of generated slag and also to the stabilization of the composition of slag generated through hot metal pre-treatment (Takahashi, 2002). This fertiliser, developed by adding potassium to the desiliconization slag, dissolves with difficulty in the water and slowly dissolves in the weak citric acid released by plant roots. The potassium contained into this fertiliser is slowly released and is effectively adsorbed by plant. The process consists in the desiliconisation process of the hot metal and subsequently the potassium carbonate ($K_2CO_3$) is continuously added into the ladle containing the hot metal (Fig. 4). Then the uniformly melted slag, that is recovered from the hot metal ladle, is solidified by cooling and crushed into a granular form. This fertilizer has been demonstrated to be as effective as other commercial potassium silicate fertilisers and combined potassium chloride-calcium silicate fertilisers when it was applied to some vegetables, in particular to rice. Its marketing started in December 2001 in Japan.

As described above, since the silicon fertilisation has been turned out to be beneficial for plant growth, such as rice and sugar cane, the identification the most promising and potential available Si sources to plant has been studied. In particular, in a greenhouse experiment several Si sources have been evaluated in order to test their ability to supply Si to rice crops. Among different Si-rich materials, metallurgical slags have been evaluated, because the high temperatures used in ironmaking and steelmaking processes release Si from crystalline form to reactive and as consequence more soluble forms, with the result to supply it to plants (Pereira et al., 2004). In the comparative study differences between silicon sources in relation to Si uptake have been observed. Furthermore steel slags (LD, AOD, electric, and stainless steel furnaces) have shown higher Si availability than BF slag, and differences depending on the type of steel produced and on the type of furnace used to produce steel. Phosphate slags provided the highest Si uptake.

On the other hand, recent studies have shown that Si concentration is negatively related to As content in straw and polished rice, that is Si in the soil available for plant reduces the uptake of As (Bodgan & Schenk, 2009).

## 4. Use of steel slags for metal stabilization in contaminated soils

Some investigations about the addition of steel slags in contaminated soils have been carried out. The stabilization technique is based on the incorporation of amendments, in order to minimize metals and metalloids, such as As, Cr, Cu, Pb, Cd and Zn that can be found in contaminated soils at wood treatment plants. In particular, when the copper sulphate and chromate copper arsenate are used to protect wood from insects and fungi, they can cause the soil phytotoxicity. While the As can be stabilized by sorption on Fe oxides and also by the formation of amorphous Fe (III) arsenates, the Cr immobilization takes place through Cr reduction from Cr (VI), which is mobile and toxic, to Cr (III), which is stable. The Cu stability in soil is pH dependent, because its mobility increases with decreasing pH. Carbonates, phosphates and clays can reduce the mobility and availability of Cu in soil. The proposed mechanism consists in precipitation of Cu carbonates and oxy-hydroxides, ion exchange and formation of ternary cation–anion complexes on the surface of Fe and Al oxy-hydroxides. While Pb can be stabilized by using phosphorus-containing amendments, that reduce the Pb mobility, Zn can be immobilized in soil by using phosphorus amendments and clays (Kumpiene et al., 2008, as cited in Negim et al., 2009). To this aim some chemical and mineralogical agents, such as industrial by-products have been applied. For instance, the use of alkaline materials, organic matters, phosphates, alumina-silicates and basic slag has been shown to limit the accumulation of Cu in plants cultivated in Cu-contaminated soils.

Among recent studies, the use of slag with basic properties into a Cu-contaminated soil has led to relevant results in soil composition (Negim et al., 2010). Because of its Ca and P content, the basic slag, on one hand, is a fertiliser, as it improves the physico-chemical properties of the soil and by increasing plant growth; on the other hand, it is a liming material, as it increases the precipitation and sorption of metals such as Cu. For this reason the investigation concerned the effects on soil pH, soil conductivity, plant growth and chemical composition of bean plants (*Phaseolus vulgaris*) in pot experiments, by mixing soil with increasing basic slag addition rates, from 0% to 4%, in controlled conditions. This material affects the soil solution composition through acid-base, precipitation and sorption reactions. On the other hand, the foliar concentration can be influenced by soil solution changes, competitions for root uptake and root-to-shoot transfer. In particular the soil pH has increased from 5.6 to 9.8, and the soil conductivity has proportionally risen from 0.14 mS $cm^{-1}$ to 0.82 mS $cm^{-1}$ by applying increasing rates of basic slag, probably due to the basic slag composition, particularly to the Ca content. Furthermore the foliar Cu concentration has probably caused a phytotoxic effect in plants grown in Cu-contaminated soil. After the basic slag addition at 1% rate the bean growth, along with the decrease of foliar Cu concentration, has been observed. Moreover while the Ca foliar concentration has increased after applying increasing rates of basic slag, the foliar P concentration has not been improved. These results suggested that the use of basic slag at 1% addition rate is effective as a liming material but, is not effective as P fertiliser. Furthermore, the basic slag addition in contaminated soil does not increase the foliar concentrations and accumulations for Cd, Cr, and Zn.

## 5. Use of slag as an iron fertilizer

The problem of iron (Fe) chlorosis can affect many crops on calcareous soils, resulting in substantial yield losses. Generally it has been corrected through the addition of Fe synthetic chelates, but these have resulted very expensive. Various studies have been focused on applying different Fe sources, in order to reduce the economic burden and to recycle some industrial by-products, such as converter slag (Wallace et al., 1982) (Sikka & Kansal, 1994). They are used not only as soil amendment but also as source of important plant nutrients, such as P, K, Mg and Fe oxides.

An investigation pursued on 1984 showed that the application of a steel by-product (dust containing 430 g Fe $kg^{-1}$) as fertilizer to alkaline soils, with o without sulphuric acid, increased dry matter yield of sorghum (Anderson & Parkpian, 1984). A similar treatment, through a mixture of sulphuric acid and iron sulphates, has allowed to correct Fe chlorosis in corn and alfalfa (Stroehlin & Berger, 1963).

While converter sludge has been used as Fe fertiliser in calcareous soils with positive results, recently the use of converter slag as source of Fe fertiliser in some calcareous soils incubation studies has led to relevant achievements. On this subject, pot experiments in a greenhouse have been carried out in China (Wang & Cai, 2006). Relevant results of this study have shown that the use of moderate steel slag or acidified slag as Fe fertilizer leads to the increase in Fe uptake and corn dry matter yield. This phenomenon is proportional to the application rate and is enhanced by the acidification of slag, although increasing application rates do not produce further improvements in yield and in Fe uptake. This suggests a possible optimized rate of these applied substances. On the other hand, in experiments conducted with the sandy loam dry matter yield significantly decreased. This can be explained because the Fe availability decreases with salt levels increase, resulting in a yield decrease and an increase of chlorosis in plants.

Although further studies still have to be conducted in order to investigate the correct rates of converter slag for different crops and its possible residual environmental impacts to the soil, important results have been achieved by using this by-product as a source of available Fe (Torkashvand, 2011). In an incubation study, by adding to the soil converter slag (from Isfahan steel factory, Isfahan, Iran), containing about 24% of Fe oxides, along with elemental sulphur and organic matter, the soil pH has increased, due to the alkaline pH of slag. But during the incubation time the pH decreased. This can be due, according to some previous studies, either to the precipitation of the free carbonates as calcium carbonate (Abassapour et al., 2004) or to the hydrolysis of $Fe^{3+}$ in the soil (Rodriguez et al., 1994). The decrease of soil pH probably results from the decomposition of organic matter applied and subsequent organic acids and $CO_2$ release as well as the buffering ability of the calcareous soils. The observed yield increase in these soils may be due to the some nutrients availability as a consequence of pH increase.

The converter slag application has proportionally increased ammonium bicarbonate-diethylenetriamine pentaacetic acid (AB-DTPA) extractable Fe, although in some incubation soils Fe extractable decreased, maybe due to the temporary fixation of iron by organic matter. Further in the pot experiment converter slag has been shown to be very effective in correction of Fe chlorosis in calcareous soils.

## 6. Recovery of phosphorus from steelmaking slags

Phosphorus is an essential element not only for plants and animals but also, along with nitrogen (N) and potassium (K), for fertilisers production. Nevertheless P has a detrimental effect on steel, by reducing the low-temperature toughness of iron and steel products. For this reason during the hot metal pre-treatment and in the steelmaking processes the dephosphorisation process takes place. The result is that most of the phosphorus in hot metal, originating from raw materials (e.g. iron ore and coal), is removed through the steelmaking slag.

The requirement of reducing environmental impact and disposal costs of slags has led to study and develop different strategies in order to internally recycle them. The slag recycling in steel production processes allows to realize a waste-free steelmaking process as well as the consumption reduction of iron and lime.

For its high content of lime (CaO) the LD slag can be used as fluxing material, replacing limestone, with the result that iron and steelmaking costs are reduced. Nevertheless free CaO reduces the effective use of LD slag, because this compound makes low hydraulic properties of slag. However the slag recycling in internal processes is limited, due to its high amount of S and P (about 1-3% of $P_2O_5$ content in the converter slag) that negatively affect them. These values are too high for using it into sinter process (where fine grain raw material is processed into coarse grained iron ore sinter for charging the BF), BF and in pre-dephosphorisation process; on the other hand they are too low for slag use as phosphatic fertiliser. Therefore some studies have been carried out in order to remove phosphorus from steelmaking slag. One of them concerns a waste-free steelmaking process in which the slag is recycled within the steelmaking process and a slag containing high phosphorous is produced and it is suitable as fertiliser (Li et al., 1995). This study has been carried out as a process modelling, by computer simulations from the thermodynamic perspective and mass balance, and results indicate the possibility to develop this process inside steelworks. The proposed steelmaking route mainly consists in a de-siliconisation process in the De-Si furnace of hot metal produced in the blast furnace and in a de-phosphorisation process in the De-P furnace before the refining into the conventional converter. The process is outlined as follows and shown in Figure 5:

- The whole slag produced into the converter (at 1923K), is totally returned to the Pre-De-P furnace, where the hot metal is dephosphorised;
- The whole slag from the Pre-De-P furnace (at 1623K) is transferred to the Regenerator;
- The Regenerator (at 1873K) contains the carbon-saturated hot metal and the most of the phosphorous is transferred from the slag to the hot metal;
- The hot metal containing phosphorous is transferred from the regenerator to the De-P-II unit (at 1623 K), which contains hot metal and synthetic slag. The phosphorous is transferred from the hot metal to this slag, by obtaining the final slag, which contains more than 10% of P and thus it can be used as fertilizer;
- A part of dephosphorised slag from the regenerator is transferred to the Pre-De-P furnace and the remainder to the De-Si furnace;
- The slag from the De-Si furnace (at 1623K) can be used in the sinter plant or in the blast furnace.

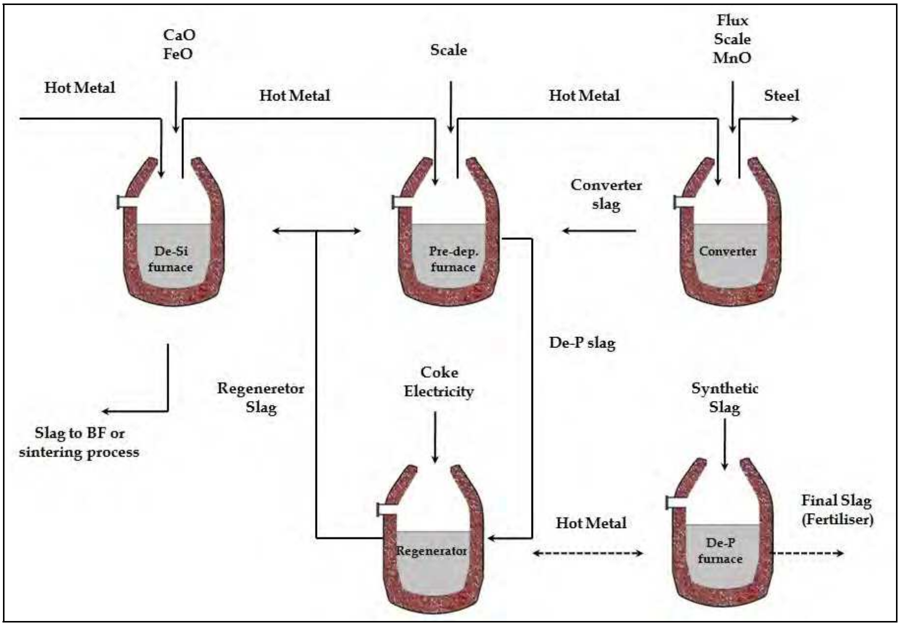



Fig. 5. Proposed method of converter slag utilization (Li et al., 1995).

The simulation results of the proposed process show that it is possible to develop a waste-free steelmaking process, through the internal slag recycling. The slag obtained in the de-siliconisation furnace can be used into the BF and/or into the sinter plant, due to its low content in phosphorus ((mass% P) = 0.48). The slag resulting from the de-phosphorisation furnace, with high P content (about 10%), can be used as fertiliser. The simulation results show that steel with low P content could be produced and that the slag generated in each unit could be completely recycled. The energy required for regenerator reactions is supplied by electric power and the total energy required is 130 kWh/t; the lime consumption is about one half of the current process. The proposed method of converter slag utilisation could allow the whole slag recycling (by thus reducing its environmental impact and contributing to save natural resources) and the production of slag with a high P content, that will be available for fertilising use.

Among different studies concerning phosphorus recovery from steelmaking slag, a research conducted in Japan, based on a method using a strong magnetic field, has been implemented for the separation and recovery of crystalline phases containing P from steelmaking slag (Yokoyama et al., 2007).

The phases of hot metal pretreatment slag, resulting by the composition analysis, can be subdivided, as follows:

- *phase A*, where P is concentrated at 10% or more and hardly any Fe content;
- *phase B*, that is composed mainly of Ca and Si, with a few percentage of P and hardly any Fe;
- *phase C*, which is composed closely to pure FeO;
- *phase D*, that is composed of CaO-$SiO_2$- FeO.

Thus the pretreatment slag can be subdivided in general into two groups: the crystalline phases containing P but not Fe (*phase A* and *phase B*) and the phases containing Fe but not P. Through measurements of magnetic properties of phases components, different behaviours in a magnetic field have been found. This has allowed to magnetically separate them, by applying a strong magnetic field of several teslas to the crushed slag.

The P recovery has resulted in obtaining a raw material for the production of fertiliser in the chemical industry. On the other hand the slag obtained after P recovery is used as building material, for roads construction and can be recycled in sintering process. Therefore the expected results of the magnetic separation method will have positive effects on environment, by reducing the generation of slag and $CO_2$ emissions and by reducing natural resources exploitation and landfill consumption. Moreover, the implementation of this technology can allow the use of iron ore with a higher P content, which is cheaper, and thus it will produce substantial economic benefits.

## 7. Environmental concerns about the slags use in agriculture

According to its environmental policy, the European targets concern the environment preservation, protection and its quality improvement, the human health protection and the efficient use of natural resources, by adopting measures for handling environmental issues on global and local level. The use of slags has a crucial significance as regard the environmental aspects. The main problem concerning the utilization of steel slags in agriculture consists of the possible leaching of heavy metals.

Heavy metals are broadly distributed in the Earth’s crust and some of their chemical forms can be a potential risk to biosphere, in particular to the water life, because of their solubility. Their bioavailability depends on the plants ability to uptake them from soil and water, due to the secretion by plants roots of chelators compounds; furthermore many heavy metals are transported by sulphur ligands, such as glutathione, and organic acids. Moreover some heavy metals are insoluble and they often interact with soil particles, and therefore they are not available to plants (Babula, P., et al., 2008).

Chromium (Cr) is used in different industrial field of applications such as steel industry, wood preservatives, electroplating, metal finishing, leather tanning, textiles and chemical manufacture and it is a frequent contaminant of both surface ground waters. In oxidizing conditions is highly soluble and forms Cr(VI) anions, such as chromates $CrO_4^{2-}$ or dichromates $Cr_2O_7^{2-}$. Under reducing conditions, through a process involving a chemical reduction and a precipitation, Cr(VI) converts to Cr(III) that is insoluble. Both forms are stable in the environment. The roots plants can absorb both forms $Cr^{3+}$ and $CrO_4^{2-}$, but, according to some date, the Cr(III) forms stable compounds (e.g. hydroxides, oxides and sulphates). Therefore it is less soluble and, consequently, less bioavailable (Srivastava et al., 1994, as cited in Babula, P. et al., 2008). However Huffman et al. has shown as there are not uptake differences between Cr(III) and Cr(VI) by bean (*Phaseolus vulgaris, Fabaceae*) and wheat (*Triticum aestivum, Poaceae*).

Although Cr is an essential element for animal and human health, hexavalent Cr salts have toxic and carcinogenic effects. The plant mechanism of toxic effect of Cr is due to the reaction between Cr-complexes and hydrogen peroxide that produces hydroxyl radicals. They can trigger off DNA alteration (Shi & Dalal, 1990a, b, as cited in Babula, P. et al., 2008), by affecting, for example, its replication and transcription.

Among heavy metals, steelmaking slags contain Vanadium (V). The V content in the processed ore is about less of 2%. During the blowing process into the LD converter the V is transferred to the converter slag as $V_2O_5$ (about 5%), which represents the main source for some procedures aiming to extract V from LD converter slag. Due to its heavy metals content and the environmental problems resulting to their release to earth, LD slag is often subjected to treatments, aiming to extract these harmful but also precious elements from it. Because of its physical properties, such as high tensile strength, hardness, and fatigue resistance, V is used in ferrous and non-ferrous alloys. For all these reasons it is desirable to recover this valuable element.

Among some studies about this topic, a recent research aims to investigate on the extraction procedure of V by using salt roasting and sulphuric acid leaching and how some leaching parameters, such as particle size, acid concentration, reaction temperature and solid:liquid ratio (S/L), may influence the kinetics process (Aarabi-Karasgani et al., 2010). The found optimum condition of leaching allows to achieve a maximum V recovery of 95%. Furthermore the size fraction of below of 0.850 mm has shown to be mostly effective in order to attain the maximum extraction. Two leaching stages have been proposed: the first one (the first 15 minutes), when the V leaching is faster, and a second stage (more than 30 min), when the leaching becomes slower. In addition, the leaching rate is controlled by chemical reaction at low temperature while at high temperature it is controlled by the solid product diffusion.

The increasing interest concerning the slags use for soil conditioning has focused the attention on the heavy metal concentrations in these materials. Several investigations carried out in Finland have shown that the concentration of some elements, such as Cr and Zn, are low because of the high temperatures of the processes. On the other hand, long-term experiments in Germany have shown that the application of steel slag as liming material does not increase the content of mobile chromium into the soil and, after using steelmaking slags as fertiliser, significant increases in Cr content have not been found in plants (R. Hiltunen & A. Hiltunen, 2004).

Nevertheless it is important to carry out further investigations focused on the heavy metals behaviour on the soil in order to better understand the effects of long-term use of steelmaking slags in agriculture. In the above-mentioned research project (Kühn et al., 2006), the preliminary investigation, based on the origin of heavy metals in the BF-BOF route, has led to the result that Cr is originated from ore, but it is also influenced by the scrap used, whereas V content is only affected by the iron ore input in the BF. In the second part of the investigation, the analysis of long term effects of Cr and V has showed significant accumulation of their content in the cultivated layer of the soil, after application of converter slag.

Results on soil analysis have shown that the highest values for Cr and V have been detected during the 50 years test conducted in St. Peter site (Black Forest), after using of basic slag, where Cr has increased of 40-50 mg Cr/kg of aqua regia soluble and total Cr, whereas V has increased of 60-70 mg V/kg of aqua regia soluble and 63-80 mg V/kg of total V.

It has been shown that both Cr and V, even though they have increased in the top soil, they are stable and immobile in the soil. In addition, after more than 50 years tests, they did not move into the deeper soil and therefore they cannot adversely affect the groundwater and consequently the human and animal health.

Plant analysis conducted in pot experiments have shown no significant differences for Cr and V uptake, but in different crops they have shown different results for Cr and V. In particular, the Cr concentrations in rye, rape and winter wheat was about lower of the detection limit ($< 0.035$ mg $kg^{-1}$). As far as V is concerned, it could not be measured in rye, rape, spring barley and winter wheat, while it has shown the highest concentration in potatoes after basic slag fertilisation of the Austrian field trials.

Furthermore it has been pointed out that the metals uptake by the plants is affected by the soil properties. For example the Cr and V contents into potatoes are reduced in soils with higher content of organic matter and with an heavy texture. In addition, the uptake of Cr, V and Cd by potatoes is favoured by low pH.

## 8. Conclusion

The steel industry is committed to increasing the way for recycling slags generated during the steel production. Since their use as landfill material has almost reached its limit, the pressure for saving natural resources and energy has led steel industry, along with other important technological challenges, to improve and increase the recycling of this by-product. While in the past steelmaking processes were exclusively design for the production of specific qualities of iron and steel, one of the today's goals for steelmakers is to design processes to produce high quality slags, according to the market requirements. New technologies and/or the improvement of existing technologies have been investigated and developed in order to achieve the ambitious target of "zero-waste" in the incoming years. To this aim, the effective utilisation of slags turns it into high value added product and allows to improve the steel industry competitiveness. On the other hand, the sustainable use of slags contributes to natural resources saving, to $CO_2$ emission reductions and to consolidate a society founded on the recycling practice.

The use of steel slags in agriculture produces not only economic but also ecological advantages. A more effective exploitation of natural resources can be achieved in both the steelmaking processes and in the agriculture. Obviously soil fertilisers have to supply nutrients, but should not have negative effects on the environment and on the human, animal and plant health. Therefore many studies have been particularly focused on the behavior and immobilization in the soil of the main heavy metals (e.g. Cr and V, contained in converter slag at higher concentrations), in order to achieve a more effective and sustainable use of steel slags in agriculture and thus improve its recycling.

## 9. References

Aarabi-Karasgani, M., Rashchi, F., Mostoufi, N. & Vahidi, E. (2010). Leaching of vanadium from LD converter slag using sulfuric acid. Hydrometallurgy, Vol. 102, No. 1-4, pp. (14-21), ISSN 0304-386X

Abbaspour, A., Kalbasi, M., & Shariatmadari, H.. (2005). Effect of Steel Converter Sludge as Iron Fertilizer and Soil Amendment in Some Calcareous Soils. *Journal of Plant Nutrition*, Vol. 27, No. 2, pp. (377 – 394), ISSN 0190-4167

Ali, M.T. & Shahram, S.H. (2007). Converter slag as a liming agent in the amelioration of acidic soils. International Journal of Agriculture and Biology, Vol. 9, No. 5, (2007), pp. (715-720), ISSN 1560-8530

Anderson, W.B. & Parkpian, P.(1984) Plant availability of an iron waste product utilized as an agricultural fertilizer on calcareous soil. *Journal of Plant Nutrition*, Vol.7, No.1, pp.(223–233)

Babula, P., Adam, V., Opatrilova, R., Zehnalek, J., Havel, L. & Kizek, R. V. (2008). Uncommon heavy metals, metalloids and their plant toxicity: a review. Environmental Chemistry Letters, Vol. 6, No. 4, pp. (189-213), ISSN 1610-3661

Besga, G., Pinto, M., Rodríguez, M., López, F. & Balcázar, N. (1996). Agronomic and nutritional effects of Linz-Donawitz slag application to two pastures in Northern Spain. Nutrient Cycling in Agroecosystems, Vol. 46, No. 3, (1996), pp. (157-167), ISSN 1385-1314

Bialucha, R., Merkel, T. & Motz, H. (2011) European environmental policy and its influence on the use of slag products, Proceeding of the Second International Slag Valorisation Symposium, Leuven, Belgium, April 18-20, 2011

Bogdan, K., Schenk, M. K. (2009). Evaluation of soil characteristics potentially affecting arsenic concentration in paddy rice (Oryza sativa L.). Environmental Pollution, Vol. 157, No. 10, (2009), pp. (2617-2621), ISSN 2617-2621

Branca, T.A., Colla, V. & Valentini, R. (2009). A way to reduce environmental impact of ladle furnace slag. *Ironmaking & Steelmaking*, Vol.36, No.8, (November 2009) , pp. (597-602(6)), ISSN 0301-9233

Conference of the Parties, 1997. Kyoto Protocol to the United Nations framework convention on climate change. Report of the Conference of the Parties, Third Session, Kyoto, 1–10 December, FCCC/CP/1997/L.7/Add.1, http:/www.unfccc.de.

Das, B., Prakash, S., Reddy, P.S.R. & Misra, V.N. (2007). An overview of utilization of slag and sludge from steel industries. *Resources, conservation and Recycling*, Vol.50, No. 1, (2007), pp. (40-57), ISSN 0921-3449

Dippenaar, R. Industrial uses of slag – The use and re-use of iron and steelmaking slags, *Proceedings of VII Intenational Conference on Molten Slags, Fluxes and Salts,* ISBN 1–919783–58–X, The South African Institute of Mining and Metallurgy, 2004

Directive 2006/12/EC of the EuropeanParliament and of the Council of 5April2006 on waste

Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives

Drissen, P., Ehrenberg, A., Kühn, M. & Mudersbach, D. (2009) Recent Development in Slag Treatment and Dust Recycling. steel research international, Vol. 80, No. 10, (October 2009), pp. (737-745), ISSN 1869-344X

EC (2001), Integrated Pollution Prevention and Control (IPPC) – Best Available Techniques Reference Document on the Production of Iron and Steel – December 2001, European Commission, Brussels

EC (2006), Commission of the European communities, regulation (EC) no 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation,Authorisation and Restriction of Chemicals(REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC,93/67/EEC, 93/105/EC and 2000/21/EC,Available from: http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32006R1907:en:NOT

EC (2009), Integrated Pollution Prevention and Control—Draft Reference Document on Best Available Techniques for the Production of Iron and Steel – July 2009, European Commission, Brussels

Eloneva, S., Puheloinen, E.-M., Kanerva, J., Ekroos, A., Zevenhoven, R. & Fogelholm, C.-J. (2010). Co-utilisation of $CO_2$ and steelmaking slags for production of pure $CaCO_3$ - legislative issues. Journal of Cleaner Production, Vol.18, No. 18, (2010), pp. (1833-1839), ISSN 0959-6526

Euroslag (2006) Legal Status of Slags. Position Paper. January 2006. The European Slag Association - *EUROSLAG*. Duisburg, Germany

Geiseler, J. (1996). Use of steelworks slag in Europe. *Waste management*, Vol. 16, No. 1-3,(1996), pp. (59-63), ISSN 0956-053X

Hiltunen, R. & Hiltunen, A. (2004). Environmental aspects of the utilization of steel industry slags, *Proceedings of VII Intenational Conference on Molten Slags, Fluxes and Salts,* ISBN 1–919783–58–X, The South African Institute of Mining and Metallurgy, 2004

Jamali, S. F. K., Forghani, A. & Shirinfekr, A.(2006).Effect of Steelmaking Slag and Converter Sludge on Some Properties of Acid Soil under Tea Planting, Proceeding of 18th World Congress of Soil Science, Philadelphia, Pennsylvania, USA, July 9-15, 2006

Kobesen, H. (2009). Legal Status of Slag Valorisation, *Proceeding of the First International Slag Valorisation Symposium*, Leuven, Belgium, April 6-7, 2009

Kobesen, H. (2010). The registration of Ferrous Slags within REACH, *Proceeding of the 6th Euroslag Conference,* Madrid, Spain, October 19-22, 2010

Kühn, M., Spiegel, H., Lopez, A. F, Rex, M. & Erdmann, R. (2006). Sustainable agriculture using blast furnace and steel slags as liming agents, European Commission, ISBN 92-79-01702-0, Luxembourg, INTERNATIONAL

Li, H.-J., Suito,H. & Tokuda, M.(1995).Thermodynamic Analysis of Slag Recycling Using a Slag Regenerator. *ISIJ Intenaltional*, Vol. 35, No. 9 (1995), pp.(1079-1088), ISSN 0915-1559

Motz , H. & Geiseler, J. (2001). Products of steel slags an opportunity to save natural resources. Waste Management. Vol. 21, No. 3, (2001), pp. (285-293), ISSN 0956-053X

Negim, O., Eloifi, B., Mench, M., Bes, C., Gaste, H., Montelica-Heino, M. & Le Coustumer, P. (2010). Effect of basic slag addition on soil properties, growth and leaf mineral composition of beans in a Cu-contaminated soil. Journal Soil and Sediment Contamination, Vol. 19, No. 2, (2010), pp. (174-187), ISSN 1532-0383

Pereira, H. S., Korndörfer, G. H., Vidal, A. A., and Camargo, M. S. (2004). Silicon sources for rice crop, Scientia Agricola (Piracicaba, Brazil). Vol. 61, No. 5, (Sept./Oct. 2004), pp. (522-528), ISSN 0103-9016.

Rex, M. (2002). Environmental aspects of the use of iron and steel slags as agricultural lime, *Proceeding of The Third European Slag Conference*, Keyworth, Nottingham, UK, October 2002

Rodriguez, M., F. A. Lopez, Pinto, M., Balcazar, N., & Besga, G. (1994). Basic Linz-Donawitz slag as a liming agent for pastureland. *Agronomy Journal*, Vol. 86, No. 5, pp. (904-909), ISSN 0002-1962

Rozman, A., Lamut, J., Debelek, M., & Knap, M. (2007). Stabilisation of ladle refining slags with borax, *Proceedings of 5th European Slag Conference*, Luxembourg, Edited by Euroslag, Duisburg, Germany, 19th-21st September 2007, 137-145

Savant, N. K., Korndörfer, G. H., Datnoff, L. E., and Snyder, G. H. (1999). Silicon nutrition and sugarcane production: a review. Journal of Plant Nutrition, Vol. 22, No. 12 (1999), pp. (1853-1903), ISSN 0190-4167

Shamim, A. H. Khan, H. R. & Akae, T. (2008). Neutralizing capacity of basic slag in acid sulfate soils and its impacts on the solubility of basic cations under various moisture regimes. Journal of the Faculty of Environmental Science and Technology. Okayama University, Vol. 13, No. 1, (2008), pp. (67-74), ISSN 1341-9099

Sikka, R & Kansal, D. B. (1994). Effect of fly-ash application on yield and nutrient composition of rice, wheat and on pH and available nutrient status of soils. *Bioresource Technology*, Vol. 51, No.2-3, pp. (199-203), ISSN 960-8524

Stroehlein, J. L. , & Berger, K. C. The Use of Ferrosul, a Steel Industry Byproduct, as a Soil Amendment. *Soil Sci. Soc. Am. J.*, Vol. 27, No. 1, (1963), pp. (51-53)

Takahashi,T., Yabuta,K.(2002). New Application of Iron and Steelmaking Slag. NKK TECHNICAL REPORT-JAPANESE EDITION, No. 87, (2002), pp.(43-48), ISSN 0915-0536

The Japan Iron and Steel Federation – Nippon Slag Association (July 2006). The Slag Sector in the Steel Industry, Available from http://www.slg.jp/e/index.htm

Torkashvand, A. M. (2011). Effect of steel converter slag as iron fertilizer in some calcareous soils. *Acta Agriculturae Scandinavica Section B – Soil and Plant Science*, Vol. 61, No. 1, pp. (14-22), ISSN 0906-4710

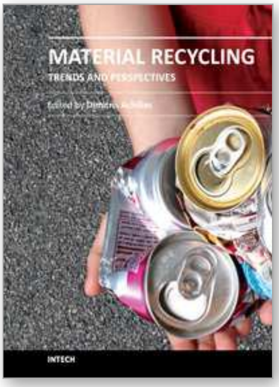
Wang, X. & Cai, Q.-S. (2006). Steel Slag as an Iron Fertilizer for Corn Growth and Soil Improvement in a Pot Experiment. *Pedosphere*, Vol. 16, No. 4, pp. (519-524)

Wallace, A., Samman, Y. S. & Wallace, C. A. (1982). Correction of lime-induced chlorosis in soybean in a calcareous soil with sulfur and an acidifying iron compound. *Journal of Plant Nutrition,* Vol.5, No.4-5, (1982), pp. (94-97)

World Steel, 2008. Sustainability report of the world steel industry. 34 pp.(Available from: http//www.worldsteel.org/pictures/publicationfiles/Sustainability%20Report%202008_English.pdf

World Steel Association, (n.d.) Available from http://www.worldsteel.org

Yokoyama, K., Kubo, H., Mori, K., Okada, H., Takeuchi, S. & Nagasaka, T. (2007)Separation and recovery of phosphorus from steelmaking slags with the aid of a strong magnetic field. *ISIJ international*,Vol.47, No.10,(2007), pp.(1541-1548), ISSN0915-1559




**Material Recycling - Trends and Perspectives**
Edited by Dr. Dimitris Achilias

ISBN 978-953-51-0327-1
Hard cover, 406 pages
**Publisher** InTech
**Published online** 16, March, 2012
**Published in print edition** March, 2012

The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.