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Industrial uses of slag—The use and re-use of iron and steelmaking slags

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Traditionally, iron ore has been reduced with coke in a blast furnace and the hot-metal product of the blast furnace containing carbon, manganese, silicon, sulphur and phosphorous, was subsequently refined in a steelmaking furnace. During ironmaking as well as during steelmaking, significant amounts of slag are produced. Two decades ago, more than 13 m tonne of blast furnace slag and 4 m tonne of steelmaking slag per annum were produced in the USA alone. It is, therefore, not surprising that many attempts have been made to re-use iron and steelmaking slags. However, these slags are not merely metallurgical waste products but, on the contrary, their compositions and physical properties are judiciously designed to optimize the operations in the respective metallurgical reactors. The variation in composition and properties of blast furnace slags are largely determined by the gangue in the ore and ash in the coke and much progress has been made in the re-use of such slag. With respect to steelmaking slag, emphasis has in recent years been placed on hot-metal treatment *before* refining and ladle treatment *after* decarburization. The bulk removal of silicon, phosphorous and sulphur from the hot-metal product of the blast furnace by specially designed slags prior to refining in a basic oxygen furnace, has reduced tap-to-tap time, lowered cost and produced steel of much higher quality. The use of synthetic slags in ladle refining techniques subsequent to decarburization in the basic oxygen furnace has resulted in reduced hydrogen and nitrogen contents and reduced solute impurities. Moreover, inclusion shape and composition control, again by the use of specially designed slags has led to the achievement of much improved mechanical properties of the steel. In these revised process routes, slag of different compositions are produced in the variety of unit processes and hence the re-use of steelmaking slags has become much more complex. Clearly, a thorough understanding of the design and use of these different slags is a pre-requisite to the development of re-use strategies. Japanese steelmakers have spearheaded attempts to reduce slag volumes in the individual unit processes and to strive towards 'slagless steelmaking' by recycling slags internally. Steelmaking slag volumes have been reduced on commercial scale from about 140 kg/tonne steel to 60 kg/tonne steel. Moreover, model predictions have shown that, in principle, all slag can be recycled and the phosphorous extracted to produce fertilizer. This development is of particular significance since the supply of low-phosphorous iron ores is diminishing at an ever increasing rate.

Keywords: slag, environment, iron, steel, recycling, blast furnace, steelmaking, ladle metallurgy, slag splashing, construction.

Introduction

Throughout the ages, slags have been used to refine metals for the benefit of humankind. For example, Agricola[1] describes the direct reduction of iron from ore: '*iron is melted out and ... when this is done, the master opens the slag-vent ... and when all has run out he allows the iron mass to cool...*' Unfortunately, most metal reduction and refining operations polluted the environment by the production of the by-products of our industrial endeavours and as a result society and the industry itself, have become seriously concerned about the environmental impact of metallurgical refining operations. Evidence of society's concern about slag wastes is to be found in a remark of Prime Minister Harold Wilson during a speech in British Parliament[2]: '*If one buys land on which there is a slag heap, 120ft. high and it costs £100 000 to remove that slag, that is not land speculation in the sense that we condemn it. It is land reclamation*'. The English novelist, Margaret Drabble handed down an even more serious indictment[3]: '*England is not a bad country... It's just a mean, cold, ugly... post industrial slagheap....*' Although some may regard this charge as the epitome of unfair comment, the question remains as to whether, by implication, we are guilty as charged and whether something can be done to eliminate, or at the very least, restrict further pollution of our precious environment. In an attempt to deal with these important questions, as far as the iron and steelmaking industry is concerned, it is instructive to briefly examine the use of slags and to inspect measures proposed and already taken, to lessen the impact of metallurgical slag generation. However, before the role of slags and slag generation can be appraised, it is necessary to inspect some important changes that have occurred in the industry and to enquire into the reasons for these changes.

Traditionally, gangue contained in the raw material charge to the iron blast furnace has been fluxed to form a liquid phase immiscible with the liquid metal product and separated as liquid slag. In the early days of blast furnace operations, some knowledge of the raw materials composition was taken into account in the design of the flux charge but operators relied mostly on experience. More recently, thanks to a much better understanding of the mechanism of slag formation and of the blast furnace process in general, slag production in different parts of the furnace can be much better designed and, as a result, slag generation can not only be controlled but also optimized and hence, mimimized[4]. In similar vein, hot-metal treatment prior to refining in a basic oxygen furnace (BOF) has led to a significant reduction in the generation of BOF slag volumes[5]. However, the total volume of slag generated in the combined steelmaking processes have to be taken into account and, for this reason, new developments in steel refining operations need to be considered.

A highly competitive steel market requires the modern steelmaker to be sensitive to customer demands in terms of product properties, quality, price and delivery. The steel industry is confronted with high fixed costs as well as expensive and sophisticated processes, which are constrained to high production rates by efficiencies and economics of scale. High costs, raw material shortages, environmental concerns and customer demands have been defined as four of the most important drivers for the steel industry[6]. The need to produce high quality steel at a competitive price has resulted in the implementation of state-of-the-art process technologies to attain ultra-high purity and ultra-cleanliness in a new generation of steels. Moreover, environmental control has likewise become a most important driver in the production of steel, to the extent that traditional production techniques have been challenged by the development of new processes and alternative production technologies. We have seen the traditional ironmaking process comprising sinter plant, coke ovens and blast furnace being challenged by the Corex, Hismelt and Dios process. One of the main aims of the new process technologies has been a reduction of the environmental impact of the coke ovens and sinter plant. The traditional steelmaking route has also been challenged by a variety of processes, of which the IRSID continuous steelmaking process and the Energy Optimizing Furnace have, perhaps, come closest to commercial reality[7]. In reaction to these challenges, steelmakers have responded by exciting and innovative developments in traditional process technologies. Most of these developments have been aimed at hot-metal treatment *before* refining and ladle treatment *after* decarburization.

The bulk removal of silicon, phosphorous and sulphur from the hot-metal product of the blast furnace prior to refining in a basic oxygen furnace has reduced tap-to-tap time, lowered cost, lowered slag volume and produced steel of much higher quality. The use of vacuum degassing subsequent to decarburization in the basic oxygen furnace has resulted in reduced hydrogen and nitrogen contents and the judicious design of slags for use in ladle refining techniques have significantly reduced solute impurities in steel. Moreover, the selective use of slag forming reagents has enabled steelmakers not only to minimize inclusion formation, but also to modify and control the shape and composition of the remaining inclusions. These practices have led to the achievement of much improved mechanical properties of steel.

A much better understanding of slags, their specific roles and functions as well as improvements in process technologies have led to a significant reduction in slag volumes generated in the iron and steelmaking industry. At the same time, the re-use of iron and steelmaking slags has been expanded, and has led to a significant reduction in the environmental impact of these by-products. Following a brief overview of the use of slags in the integrated route of iron and steelmaking, attention will be given to some measures taken to re-use these slags.

The use of metallurgical slags

The use of slag in the iron blast furnace

The dissection of quenched experimental and operating blast furnaces, especially the studies conducted in Japan[8], clarified in much more detail than before, the importance of the cohesive zone, the nature of the flow of gas through the coke slits in the cohesive zone and the nature of the chemical reactions in the blast furnace. These studies have revolutionized the very concept of the process but, unfortunately, it was not possible to determine in a quantitative manner the exact way in which slag is generated in the furnace and how slag and metal droplets interacted on their way down the furnace from the cohesive zone to the hearth[9]. Because the primary function of blast furnace slag is to absorb gangue and to act as recipient of non-metallic impurities, the composition of the slag is largely governed by the composition of the ore and ash in the coke. Consequently, a reduction in slag volume has to be accompanied by a reduction in the impurity content of the raw materials, concomitant changes in slag chemistry, process refinement and/or treatment of the liquid product of the blast furnace before refining in a steelmaking furnace. Tailoring the slag chemistry to optimize furnace operations is furthermore hampered by the presence of alkalis in the raw material. Alkali oxides are reduced to metal and the metal then evaporates in the hotter parts of the furnace, only to be re-oxidized in the furnace shaft. This alkali circulation seriously effects furnace stability and as blast furnace operators will usually give priority to furnace stability over and above other operating variables, the slag composition is usually designed to ensure effective alkali removal. Most effective for alkali removal is an acidic slag but, unfortunately, low basicity slag is exactly the opposite of what is required to ensure effective sulphur removal. Hence, a high alkali load in the charge of a blast furnace almost inevitably requires the installation of external desulphurization facilities.

The modern blast furnace is characterized by a large hearth diameter, hindering the flow of gas as well as liquid metal and slag through the deadman and hearth. The raceway penetrates to a depth of only 2 m into the furnace hearth so that the gas flow is directed to the periphery as the hearth diameter is increased and, hence, the active area decreases with an increase in furnace hearth diameter. The large inactive zone in the furnace not only affects gas distribution but also impacts on the ability to drain metal and slag from the furnace. Following discharge from the lower surface of the cohesive zone, metal and slag droplets drain through a packed coke bed (deadman) before collecting in the furnace hearth[10]. In order to ensure that slag droplets flow through the deadman and into the hearth efficiently, it is necessary to fully flux or melt these slag droplets before they enter the deadman zone. Freezing slag or unmelted ore can seriously impede the permeability of the deadman and, hence, the flow of liquids into the hearth. Nightingale[11] formulated the Deadman Cleanliness Index

(DCI) as a quantitative measure of the permeability of the deadman and has convincingly shown that this index correlates well with slag/metal partitioning in the blast furnaces of BHP Steel. Hence, this index can also provide a measure of the efficiency by which slag is created in the cohesive zone. Brämming and Wikström[4] point out that it has become increasingly important not only to study slag formation in the cohesive zone, but also to identify the location of slag creation in other parts of the furnace[12]. With reference to Figure 1, current understanding of the formation of slag in the iron blast furnace may be summarized as follows: primary slag is formed by gangue from ferrous materials; bosh slag forms by dissolution of fluxes and to a limited extent, coke ash into the primary slag; tuyere slag forms from the ash of fuels combusted in front of the tuyeres and the final slag is formed by the combination of the bosh and tuyere slag form which some oxides have been reduced. Brämming and Wikström[4] have shown that the blast furnace slag volume generated at the SSAB, Oxelösund Works has been reduced from more than 300 kg/tHM in 1974 to less than 150 kg/tHM and it seems possible that the slag volume can be even further reduced by the injection of slag formers through the tuyeres[12]. An even more effective approach would be to inject BOF-slag through the tuyeres. This technique is attractive, not only because it will provide an opportunity for the re-use of steelmaking slag, but also because the injection of highly oxidized BOF slag lowers the melting point of the fuel ash significantly, thereby rendering liquid slag in the tuyere region[13].

The use of slag in steelmaking processes

Implications of new process developments

Shortly after Bessemer introduced pneumatic steelmaking in 1856, the basic open hearth was developed and this process technology dominated steel production until the mid sixties. The top blown oxygen converter, or basic oxygen furnace (BOF) was developed in the mid 1950s and bottom-blowing facilities were later added. In the past 40 years, the basic open-hearth process has been almost completely replaced by various top, bottom or combination blowing oxygen steelmaking processes[14]. Traditionally, liquid steel has been produced in integrated steel plants, starting with iron ore and coke, or through an electric-arc furnace route by the recycling of scrap. In integrated steelmaking, the hot-metal product from a blast furnace is refined in a basic oxygen furnace and production capacities are typically in excess of five million tonnes per annum. In the electric-arc furnace steelmaking route, scrap is recycled. Typical capacities are 0.3 to 2.5 million tonnes per annum and the capital outlay of such a facility is considerably less than that of an integrated plant. In the past, integrated mills dominated the high quality steel strip market while the mini-mills produced the standard grades. The quality of steel produced by electric-arc furnace technology is restrained by the level of metallic residuals such as copper, nickel and tin present in the scrap charge. However, the use of hot-briquetted iron, directly reduced iron and liquid hot metal has significantly increased the product quality range. Most modern electric-arc furnaces use a combination of oxy-free burners, pulverized coal injection and oxygen injection to supplement electrical energy input. Today, steel production in one year exceeds that of all other metals combined in ten years of production and steel is produced in integrated plants by the basic oxygen process and in mini-mills through electric-arc furnace technology. In the USA, 60% of the steel is currently produced by means of the oxygen converter and 40% by electric-arc furnace technology as shown in Figure 2[14]. For the purposes of the present discussion, the use of slag in the iron and steel industry will be restricted to applications in integrated steelmaking.

Huge improvements in steel processing technology have been made possible through a fundamental understanding of the mechanism and rate of metal/slag/gas reactions. The Japanese steel industry has spearheaded a new trend in integrated steelmaking by removing the bulk of sulphur and phosphorous impurities from the hot-metal product of the blast furnace prior to decarburization in a basic oxygen converter. Subsequent to decarburization, hydrogen removal, final alloy trimming as well as inclusion removal and modification are achieved through a variety of secondary refining techniques. By these process modifications it has become possible to obtain better yields, produce cleaner steel and lower operating costs[15]. This modern trend in steelmaking is schematically shown in Figure 3. The introduction of hot-metal pretreatment and

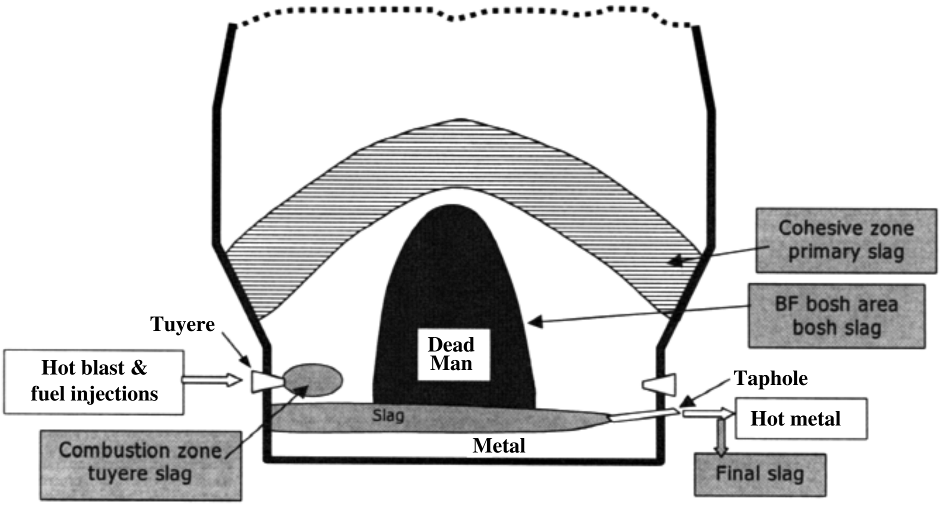

Figure 1. Formation of slag in the iron blast furnace

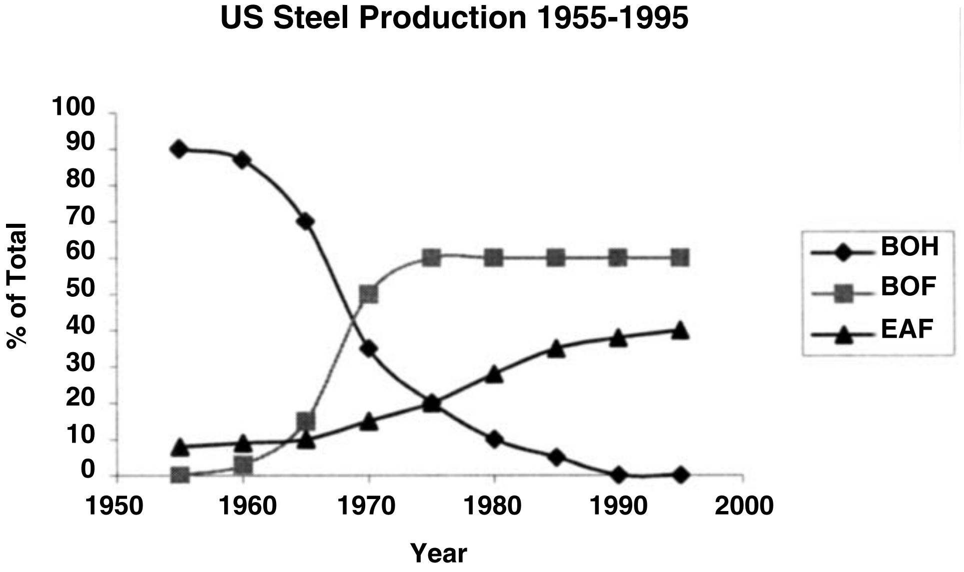

Figure 2. Steel Production in the USA by refining process. BOH = Basic Open Hearth; BOF = Basic Oxygen Furnace; EAF = Electric-arc Furnace

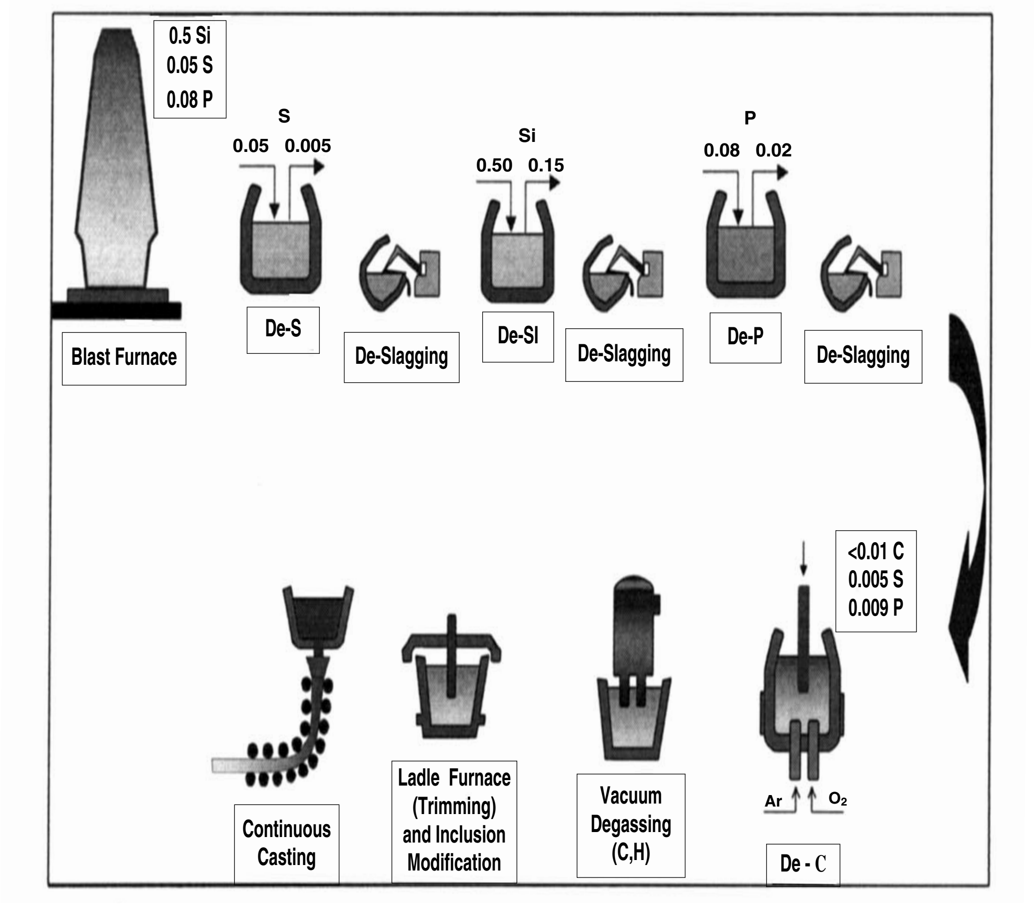

Figure 3. An example of a modern steelmaking route

ladle metallurgy has had a significant influence on the type of slags being used in the integrated steelmaking route. Hot-metal can only be dephosphorized if it contains less than 0.15% silicon and for this reason it is important to desiliconise the hot metal prior to dephosphorization. Additional advantages of the bulk removal of silicon from the hot-metal are that chemical attack on the refractory lining of the basic oxygen furnace is minimized and a minimal amount of slag-making fluxes is required, thereby maximizing process yield[16]. On the other hand, lowering the silicon content of the hot metal precludes utilization of the thermal value from silicon oxidation and, hence, reduces the scrap-melting capacity of the basic oxygen converter. Because of the economic value of the ability to melt large quantities of scrap in the BOF, external desiliconization and dephosphorization have not been adopted in the United States and many other plants[15]. In some plants, the silicon and phosphorous removal steps occur in full size oxygen converter vessels and the resulting carbon containing liquid metal is transferred, after separation of the primary process slag, into a second converter for carbon removal by oxygen blowing[16]. In this sequence, the slag from the second vessel is used as starter slag for the first step. The heavily oxidizing environment in an oxygen converter limits the sulphur removal capability of this process. Hence, the sulphur has to be removed either in the hot-metal, or subsequent to the carbon blow in the converter. It is far more costly to remove sulphur from steel and, hence, techniques have been developed to do bulk desulphurization in the hot-metal. Depending on the raw materials available the sulphur contents in hot-metal can typically vary between 0.02% and 0.2%. Through external (hot metal) desulphurization, the sulphur content is typically reduced to less than 0.01% before introduction of the hot-metal into the oxygen converter[15].

The presence of a slag/metal/gas emulsion accounts for the high speed of refining in a top-blown oxygen converter. The large interfacial areas in the emulsion are conducive to effective heat transfer and rapid reaction rates[17]. However, it also results in liquid steel containing typically 400-800 ppm oxygen and slag which contains 25% to 35% iron oxide. These highly oxidizing conditions contribute to the loss of valuable alloying elements, particularly manganese, by oxidation to the slag[15]. In a bottom-blown converter, oxygen is introduced through several tuyeres installed in the bottom of the vessel. Each tuyere consists of two concentric pipes with the oxygen passing through the centre and a hydrocarbon coolant passing through the anulus between the pipes. A new era in pneumatic steelmaking was entered into when combination blowing was introduced. This technique, that has been widely adopted for carbon steelmaking, comprises top-blown lancing and a method of stirring from the bottom. The configurational differences in mixed blowing lie principally in the bottom tuyeres or permeable elements. In the mixed (or combined) blowing vessel, the carbon-oxygen reaction proceeds closer to equilibrium because of more effective stirring, enabling controlled production of very low carbon steels without losing the advantage of the high reaction rates inherent to top-blowing. Also, the slag is less oxidized in this process, resulting in higher metallurgical yields and a substantially better recovery of manganese. In typical mixed blowing, a saving of 25% in manganese requirements can be made[15]. Provided the silicon, phosphorous and sulphur content of the hot-metal are significantly reduced before the hot-metal is charged to the converter, 350 tonnes of liquid steel can typically be decarburized in 10 minutes in a modern basic oxygen converter. Figure 4 [various sources] shows how the blowing time has been reduced from 20 to 10 minutes over the past 25 years while the tap-to-tap time has been reduced from 40 to 20 minutes in the same period.

The introduction of ladle refining, following decarburization in an oxygen converter or electric-arc furnace, has had a pronounced effect on the ability to produce clean steel. Moreover, the introduction of ladle refining techniques to electric furnace steelmaking has resulted in the electric-arc furnace being used as fast melters without the need to perform any refining in the furnace. In addition, ladle refining and degassing make it possible for the steelmaker to exert much tighter control over the properties of the final product through improved accuracy in the composition of the final product as well as its cleanliness and by being able to control inclusion morphology[18].

Slag/metal reactions

In order to put into perspective the way in which slags are used to remove silicon, sulphur and phosphorous from the hot-metal product of the blast furnace or from steel, it is instructive to briefly review the relevant reaction equilibria:

$$\text{Silicon: } [Si]+2[O]=(SiO)_2 \quad [1]$$

$$\text{Sulphur: } [S]+\left[O^{2-}\right]=\left(S^{2-}\right)+[O] \quad [2]$$

$$\text{Phosphorus: } [P]+5/2[O]+3/2\left(O^{2-}\right)=\left(PO_4^{3-}\right) \quad [3]$$

[X] refers to elements dissolved in liquid metal and (Y) to compounds dissolved in liquid slag

It follows from Equation [1] that silicon is best removed under highly oxidizing conditions. The silicon content of hot-metal is usually lowered by the injection of mill scale or sinter powder into the liquid hot-metal in the blast furnace runner, the torpedo car or transfer ladle.

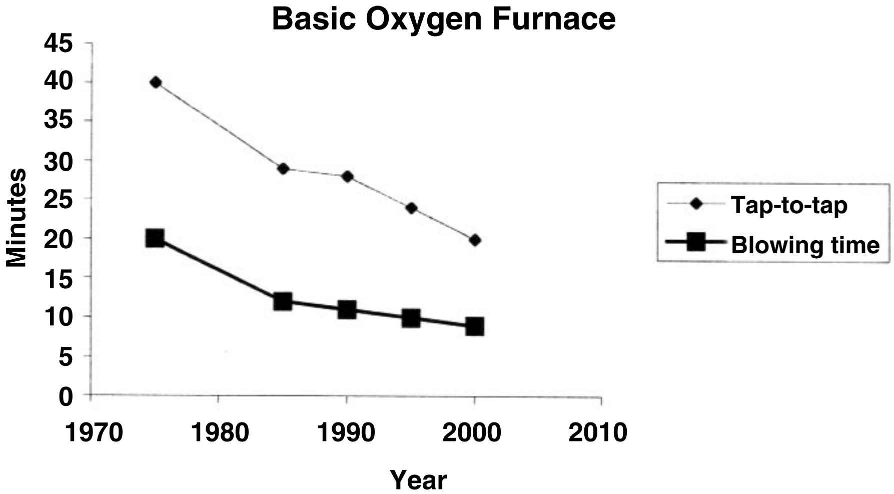

Figure 4. Reduction in tap-to-tap time and blowing time for operations in the basic oxygen furnace form 1975 to 2000 [Various sources]

Alternatively the silicon may be removed by the injection of oxygen into the torpedo or transfer ladle and in process routes where phosphorous is removed subsequent to desiliconization; the silicon concentration is lowered to less than 0.15 %. Lime may be used to flux the silica and these slags may be recycled to the sinter plant[19].

Sulphur is clearly best removed under reducing conditions such as prevail in hot-metal or when the steel has been deoxidized. However, desulphurization of liquid steel is more costly than hot-metal desulphurization and desulphurization of steel is usually confined to fine-trimming during secondary metallurgy. Equation [2] further indicates that a highly basic slag is required for efficient sulphur removal and for this reason $Na_2(CO)_3$ has extensively and very efficiently been used as a desulphurizing reagent. However, environmental concerns have forced steelmakers to seek alternative techniques. Lime and CaF_2 are often co-injected into the hot-metal, either in the torpedo car or the transfer ladle but the use of CaF_2 is also fraught with danger as far as the environment is concerned. CaC_2 injection has been used and several lime-based reagents have been developed for desulphurization of hot-metal. The effectiveness of basic slag to act as a desulphurizer, is often measured by the sulphide capacity Cs, where the sulphide capacity is defined as[20]:

$$C_s = (Mass\%S)(P_{O2})^{1/2} / (P_{S2})^{1/2}$$

The sulphide capacity, C_s correlates well with optical basicity and hence slag compositions conducive to desulphurization can be determined from knowledge of the optical basicity of the individual components[21]. Moreover, Lehman *et al.*[22] have demonstrated that our understanding of slag behaviour has been developed to the extent that slags with high sulphide capacity can be designed by the use of statistical thermodynamic models.

Wagner proposed that a phosphate capacity, similar to sulphide capacity be defined[23]. However, the correlation of the phosphate capacity with slag basicty is not nearly as good as that of the sulphide capacity and Turkdogan[19] has simplified Wagner's formulation to describe the practically observed phosphorous distribution between metal and slag more accurately. His definition of the phosphate capacity of slag, k_{PO}, is:

$$k_{PO} = (\%P) * [\%O]^{-0.25} / [P] \qquad [4]$$

and the relationship between phosphate capacity and slag basicity is given by:

$$\log k_{PO} = 21740 / T - 9.87 + 0.071(BO) \qquad [5]$$

Where BO = % CaO + %CaF_2 + 0.3 (% MgO)

The ability of a basic slag to dephosphorize is clearly a strong function of temperature with lower temperatures, such as exist in hot-metal, favouring dephosphorization. On the other hand, Equation [3] shows that phosphorous removal is best done under strong oxidizing conditions such as exist in the BOF but, unfortunately from a phosphorous removal point of view, temperatures in the BOF, are high especially towards the end of the blow when the oxygen potential is high. Because of these conflicting requirements for the removal of phosphorous, the decision as to where phosphorous is best removed, is one of economics rather than of thermodynamics. Should phosphorous be removed in the BOF, it has to be done towards the end of the blow when the oxygen potential is high. The highly oxidized state of the slag not only leads to the obvious loss of iron, but also to excessive attack on the refractory lining of the furnace and, hence, practical considerations have led to the tendency to remove phosphorous from the hot metal rather than in the BOF, either in the torpedo car or in the transfer ladle.

Pre-treatment of hot-metal and the basic oxygen furnace

A process route that would minimize slag formation and cost whilst at the same time ensure high productivity, cannot be designed from knowledge of thermodynamics and process dynamics of the individual process steps alone. The availability of raw material, existing plant design, marketing strategy and product range as well as a host of other economic factors, each and collectively, have a determining influence on the choice of the process route. For example, US steelmakers have mostly elected not to implement hot-metal pre-treatment because they wish to use high scrap loadings in the BOF and, hence, they require a relatively high silicon concentration in the liquid metal feed to the BOF[15]. However, from an environmental point of view, pre-treatment of the hot-metal product of the blast furnace is very attractive, especially as far as slag minimization is concerned, and for this reason a process route in which the unit processes are separated will be analysed in more detail later. An example of such a process route is shown in Figure 3:

Various techniques and combinations of reagents have been used for the bulk removal of silicon from the hot-metal product of the blast furnace. For example, mill scale and lime have been added in the runner of the blast furnace; mill scale and/or sinter have been injected into the torpedo car or transfer ladle and oxygen has been blown into the torpedo car or transfer ladle. If subsequent dephosphorization is to be done, the silicon content of the hot-metal is reduced to below 0.15%. The slags produced during desiliconization contain FeO, SiO_2, CaO and MnO. Very little sulphur or phosphorous are transferred to the slag so that the slag resulting from desiliconization treatment can be recycled to sinter plants[19].

$Na_2(CO)_3$ is very effective in removing phosphorous as well as suphur from liquid hot-metal provided the silicon content of the hot-metal is low enough. Soda ash is frequently injected with nitrogen combined with co-injection or blowing with oxygen and hence slag of high basicity is provided in the presence of high oxygen activity. In addition, the reactions occur at low (hot-metal) temperatures and, hence, the conditions are conducive to the removal of phosphorous. Because the basicity of the slag is high, significant amounts of sulphur are removed simultaneously. 90 % P and 75+ % S are typically removed in such a process. A major disadvantage of the use of soda ash, is the reduction of sodium carbonate to sodium gas by the following reaction:

$$Na_2(CO)_3(l) + 2[C] = 2Na\ (g) + 3CO\ (g) \qquad [6]$$

The generation of sodium fumes constitute a health risk and has raised serious environmental concerns. For this reason, alternative reagents have been tried. For example, great success has been achieved by the injection of CaO, mill scale and CaF_2 with and without co-injection of oxygen[19]. Recycling of slags from the dephosphorization step will be discussed in more detail later.

Examples of the effectiveness of desulphurization of hot-metal, using reagents other than soda ash, are shown in Figure 5[19]. In the USA blast furnace hot-metal contains typically 0.04 % to 0.07%S while steel quality requirements

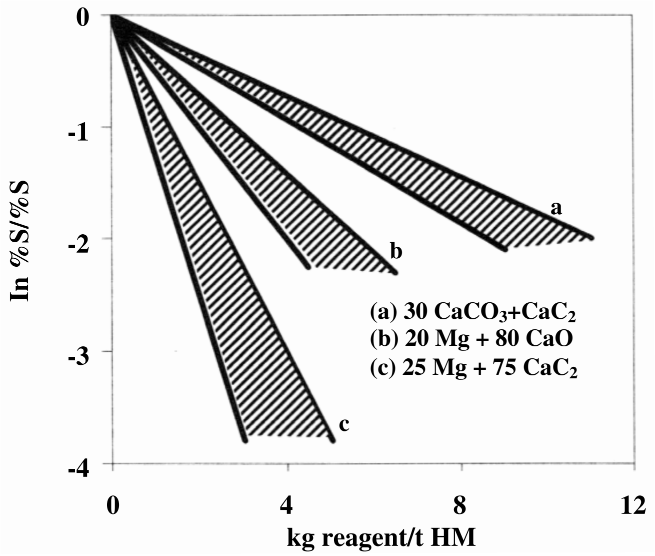

Figure 5. Examples of the effectiveness of various desulphurization reagents in the pre-treatment of hot-metal[19]

demand that the sulphur content of hot-metal charged to the BOF be lower than 0.01%S, and to produce certain steel types, as low as 0.001%S. Following desulphurization, the slag is raked off the liquid metal and 15–20 kg slag/t-HM is typically produced[24]. Although there is a possibility that the sulphur containing slags can be recycled to the sinter plant, most of the slags resulting from desulphurization is discarded.

It is interesting to note that because hot-metal produced by the Corex-process is low in silicon, lime-based reagents may be used to desulphurize and dephosphorize simultaneously Corex hot-metal. Van Niekerk[25] and van Niekerk and Dippenaar[26] have shown that additions of the order of 10–15 % of Na_2O and CaF_2 to lime-based reagents can increase the sulphide and phosphate capacities, respectively, to the extent that desulphurization and dephosphorization can be done simultaneously. Figures 6 and 7 show that the relevant capacities are high and comparable to those of Na_2O-SiO_2 slags. These slags may, of course, also be used to treat desiliconized hot-metal from the blast furnace. More recently, Yang *et al.*[27] have also shown that small additions of Na_2O and CaF_2 to calcium aluminate slags are very effective as desulphurizers of hot-metal.

Examples of the extent to which the generation of slag in the BOF-steelmaking route can be reduced by the use of hot-metal pre-treatment, is shown in Figure 8[6]. Japanese steelmakers have reduced the slag production in the BOF steelmaking route from 138 kg/t-steel to 121 kg/t by the introduction of desiliconization and dephosphorization. The typical slag production in the BOF itself was reduced from 92 kg/t to 43 kg/t in the period 1984 to 1995. More recent attempts to reduce the slag volume in the BOF has resulted in a reduction of the the total slag volume to 60 kg/t and slag production in the BOF unit of only 10 kg/t-steel[28]. The separation of desulphurization and dephosphorization from the BOF unit and the concomitant optimization of these refining steps, combined with extensive desiliconization of the hot-metal, has led to significant improvements in productivity as shown in Figure 4. In this process route the BOF unit is essentially used as a decarburizer only and, hence, the high productivity. Elimination of dephosphorization in the BOF (which requires a high FeO content in the slag), has the further advantage that the refractory life of the BOF unit is significantly increased.

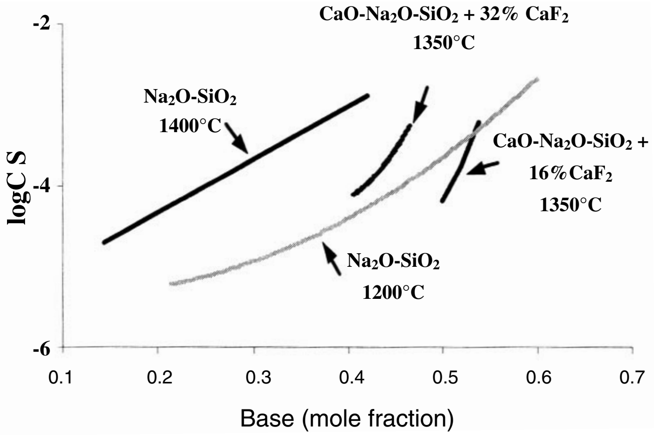

Figure 6. Sulphide capacities of various slag systems[25]. Na_2O-SiO_2-data after Chan and Fruehan[42]

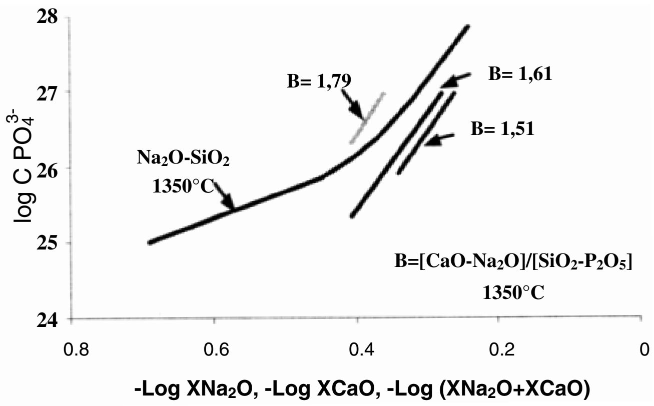

Figure 7. Phosphate capacities of different slag systems[26]

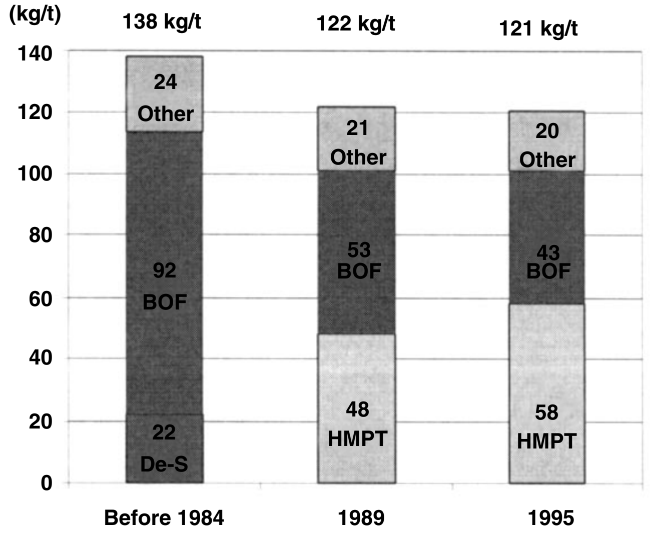

Figure 8. Reduction in the production of slag in the BOF-stseelmaking route by the introduction of hot-metal pre-treatment[6]

Secondary metallurgy

The introduction of ladle refining, following decarburization in an oxygen converter or electric-arc furnace, has had a pronounced effect on the steelmaking process. Moreover, the implementation of ladle refining has enabled electric furnace steelmakers to use their furnaces as fast melters without the need to perform any refining in the furnace. In addition, ladle refining and degassing make it possible for the steelmaker to exert much tighter control over the properties of the final product through improved accuracy in the composition of the final product as well as its cleanliness and by being able to control inclusion morphology[18]. A variety of ladle refining techniques, collectively known as secondary metallurgy has been developed over the years to replace, at least in part, the conventional addition of deoxidants and other alloy additions to liquid steel on tap (from the BOF or EAF). In these ladle refining techniques, the temperature of the melt is controlled; final decarburization and deoxidation are done and hydrogen is removed from the liquid steel through vacuum treatment. Sulphur and phosphorous are removed in the ppm range through the use of synthetic slags and compositional adjustments are made by trimming with ferro-alloys. Finally, and importantly, inclusion removal are accomplished by argon bubbling and slag rinsing and the morphology of inclusions is modified by calcium treatment.

Deep desulphurization, reducing the sulphur content in the liquid steel to below 20 ppm., is done under strong reducing conditions, usually with $CaO\text{-}SiO_2\text{-}Al_2O_3$ slags in the presence of aluminium or by the injection of $CaO\text{-}CaF_2$ powder. Sulphur distributions of up to 1000 can be achieved in these slags[18]. The governing reaction is:

$$2/3[Al]+[S]+(CaO)=(CaS)+1/3(Al_2O_3) \qquad [7]$$

Phosphorus distribution ratios of more than 1000 can be achieved by the addition in the ladle of $CaO\text{-}FeO\text{-}SiO_2$ slags containing small amounts of MnO and Na_2O[18].

Lastly, it is interesting to refer briefly to the use of micro-slags to control inclusion morphology and sulphide shape control. By the injection of calcium into deoxidized and desulphurized slags, solid alumina inclusions are converted to liquid calcium aluminates that float much easier out of the steel. Moreover, calcium aluminate inclusions retained in liquid steel, suppress the precipitation of MnS stringers during solidification. Small, globular calcium aluminates, covered by a layer of CaS form and even if they do not float out, they are less detrimental to the mechanical properties of the solidified steel[29]. Göransson *et al.*[30] have shown in a convincing manner that the composition of synthetic slag used in the ladle furnace to remove inclusions in bearing steels, influences the inclusion type and inclusion size distribution. A high value of CaO/Al_2O_3 is conducive to lowering the activity of alumina in the slag and, hence, to favour the removal of solid alumina inclusions.

Slag splashing

Slag splashing is a technology which uses high pressure nitrogen through the oxygen lance of the BOF after tapping the liquid metal and splashes the remaining slag on to the refractory lining[31]. The slag coating splashed on to the refractory lining, solidifies on cooling and serves as a consumable refractory coating in the following heat. Hence, the slag coating rather than the working lining or the gunned coating is utilized as refractory protection. After the liquid steel has been tapped from the BOF, the remaining slag may be conditioned to achieve the appropriate viscosity and nitrogen is then blown through the oxygen lance under high pressure to splash the slag on to the refractory lining. At the end of the nitrogen blow, the furnace is tilted and the excess slag is dumped. Alternatively, slag splashing may be done with the steel and slag in the vessel. This approach is usually followed when there is a need to coat the trunnions and upper reaches of the furnace. By 1994, the use of slag splashing increased the lining life of BOF vessels at the Indiana Works of LTV, to more than 15 000 heats and the two-furnace availability increased from 78% in 1984 to 97% in 2000[32]. More recently, Liu *et al.* have provided a physical modelling study in an attempt to assist in the design and optimization of the splashing technique[33].

It is interesting to note that although the technique of slag-spalashing has already been adopted as standard operating practice in many steelmaking shops, it is also one of the best examples of the effective and economical re-use of steelmaking slag.

Re-use of slag

Background

Whether or not iron and steelmaking slags should be considered as by-products, or wastes of the iron and steelmaking process or, alternatively, whether it should be considered as renewable virgin material in the sense that it is a new and useful material that has not been used before, may be an interesting point of debate but, whatever the outcome of the debate, economic and environmental concerns demand that these slags be used more effectively than in the past.

The principal constituents of blast furnace slag are the oxides of silica and alumina originating mainly from the iron bearing material, lime and magnesia which have been added as flux. Slag is tapped from the furnace at a temperature of about 1480°C and, depending on the manner in which the slag is cooled, distinct types of blast furnace slag can be produced: air-cooled, expanded or granulated[34]. Air-cooled slag is produced by allowing blast furnace slag to run into a pit adjacent to the furnace or is transported in ladles and dumped into a pit. Solidification of slag then occurs under the prevailing atmospheric conditions. Treatment of molten blast furnace slag with controlled quantities of water accelerates solidification and produce a lightweight product. Granulated slag is produced by quenching the liquid slag from the blast furnace by a stream of water at a rate sufficient to ensure that no crystallization occurs[34]. These slags have been put to many commercial uses such as railroad ballast, aggregate in concrete products, manufacture of Portland and slag cement. In the USA, air-cooled slag has been used extensively as an aggregate in concreting operations. Expanded slag has been used in aggregate in the manufacture of lightweight concrete for structural purposes, floor fills and masonary units. Granulated slag has, in the past, been used for the manufacture of cement, construction of highway bases and for soil conditioning[34].

Before the introduction of the pre-treatment of hot-metal, steelmaking slags with their high iron and manganese contents have frequently been used in the blast furnace burden. In this way almost all the iron is recovered and 70% of the manganese is reduced into the hot-metal. Also, because steelmaking slags contain more lime than is required to flux the impurities present, this lime will flux the acid impurities contained in the iron-bearing burden and the coke ash. The main limitaton to the use of steelmaking slag in the blast furnace is the phosphorous content of the slag since virtually all the phosphorous present in the slag will be reduced into the hot-metal[34]. In their analysis of the use of steelmaking slag in Canada, Murphy *et al.*[35], point out that steelmaking slag has been used mainly for aggregate in road bed construction or as a substitute for gravel, but these applications do not provide added value for the steel manufacturer. Moreover, the high content of free lime and magnesia is detremental to the volume stability of steel slags when used as aggregate, causing concern in the use of steel slags for this purpose. Murphy *et al.*[35], sought to adjust the composition of steelmaking slag to make it suitable for blending with conventional Portland cement clinker and found experimentally, that this goal can be achieved by small adjustments of the slag chemistry. By oxidizing FeO in the slag to Fe_2O_3 and by rapidly quenching the slag with water, they produced a predominantly glassy material that possessed inherent cementitious potential. Reeves and Lu[36] have also studied the possibility of modifying steelmaking slag to render volumetrically stable aggregate. They found that the adddition of Fayalite to molten steelmaking slag inhibits the precipitation of free lime during solidification on cooling, making it much more acceptable as aggregate. Hiltunen[37] emphasises that, traditionally, the expansion problem has been overcome by allowing the slag to age outdoors but that significant economic penalties are incurred by the use of this technique. However, a new technique has been developed on commercial scale by which oxygen and silica are injected into the molten slag when it is drawn off.

Slag resulting from the pre-treatment of hot-metal and slag formed during secondary steelmaking vary greatly in composition. Because of their heterogeneous properties and relatively small volumes, little research has been done to re-use these slags efficiently and, in the result, these slags are mostly used in landfill applications[37].

A case study of slag utilization in the construction industry

In an attempt to paint a picture of how iron and steelmaking slags are currently being utilized, the specific use of these slags in Ausralia and New Zealand will be briefly reviewed[38–40]. Table I shows that a little more than 3 million tonnes of various forms of slag have been produced in these two countries in the year 2000 and in the Table a breakdown is given of the origin of these slags. Blast furnace slag (1.75 mt) and steelmaking slag (0.8 mt) constitute by far the largest volume of slag produced. Blast furnace as well as Basic Oxygen Furnace slags are produced at the Port Kembla Works of BHP Steel and at the Whyalla Works of Onesteel. Electric-arc Furnace slag is produced in Melbourne, Sydney and Newcastle.

The production and utilization of iron and steelmaking slags are more specifically outlined in Table II. Out of a total mass of 2.705 mt, 2.344 mt (or 86%) are utilized for various purposes and it is instructive to consider the production and utilization of these slags in more detail.

In the Australian operations, liquid blast furnace slag flows into pits where it is predominantly air cooled and sprayed with a small quantity of water. Alternatively, liquid slag is rapidly quenched using large volumes of high-pressure water to produce a sandy material called granulated blast furnace slag. In the Basic Oxygen and Electric-arc Furnace Processes, liquid steel and slag are separated on completion of the refining of the steel; the

Table I
Total slag production in Australia and New Zealand in the year 2000[38]

Origin	Blast furnace		Basic oxygen furnace	Electric-arc furnace	Other
	Air Cooled slag	Granulated slag			
Mass Produced	1 050 000	700 000	800 000	155 000	360 000
% Produced	34	23	26	5	12

Table II
Production and utilization of blast furnace and steelmaking slag in Australia and New Zealand in the year 2000[38]

Slag type	Blast furnace	Granulated blast furnace	Basic oxygen furnace	Electric-arc furnace
Production (t)	1 050 000	700 000	800 000	155 000
Utilization (t)	750 000	700 000	510 000	84 000
Utilization (%)	71	100	64	54
Production technique	Air cooled	Molten slag quenched with high pressure water sprays	Air cooled and watered	Air cooled and watered
Typical applications	Base, Subbase Concrete aggregate Filter aggregate Construction fill Scour protection Rockwool	Subbase Construction fill Construction sand Stabilizing binder Cement manufacture Grit blasting Reinforced earth wall infill Glass manufacture Cement replacement able to enhance concrete durability. Stabilizing binder	Sealing aggregate Asphalt aggregate Base, Subbase Construction fill Subsoil drains Grit blasting	Sealing aggregate Asphalt aggregate Base, Subbase Construction fill Subsoil drains Grit blasting

liquid slag is poured into a transfer ladle and then dumped into pits where, after solidification, the slag is cooled with water sprays and then processed into aggregates[38]. Aggregate processing is similar to the production of aggregates in any quarry. Because steelmaking slags contain free lime and magnesia, conditions conducive to hydration must be created and sufficient time must be allowed for the aggregate to fully hydrate. This is usually achieved by stockpiling the slag to allow moisture from the atmosphere to react with the free lime and magnesia and by regularly watering the aggregate to accelerate the hydration process. After conditioning and weathering, aggregates may be blended in various combinations. Metallic particles, trapped in the slag, are separated during processing in purpose built metal recovery plants.

Blast furnace as well as steelmaking slags have been used in pavement construction as engineering fill, subbase and base. Examples of this use are to be found in the building of several freeways, heavy road network construction and the third runway construction at Sydney Airport. Both blast furnace and steelmaking slags have successfully been used in spray sealing and asphalt applications but steelmaking slag is more commonly used as its better strength, abrasion and impact resistance make it particularly suitable for use in areas subjected to heavy vehicle loads and high shear stress[38].

Blast furnace slag aggregates have been used for concrete manufacture. Special concrete mixes need to be designed because the properties of blast furnace aggregates are different from conventional aggregates[39]. In the year 2000, 450 000 tonnes of slag aggregate and slag sand were used by the Australian concrete industry. Blast furnace slag has a chemical composition similar to that of Portland cement, although in different proportions and slag cements currently available in Australia contain 20–40% slag for general construction and 60–70% slag for applications which require reduced heats of hydration[39]. Examples of the use of slag cement and aggregate are: the Sydney harbour tunnel submerged tube units where cement containing 60% ground granulated blast furnace slag was used; pile cap foundation blocks for the Anzac bridge, Sydney; the Sydney airport link tunnel and the foundations of Blast Furnace No. 6 at Port Kembla[38]. The environmental impact of the use of blast furnace slags for cement is particularly noteworthy. The use of slag in cement represents a substantial reduction in the generation of greenhouse gases. For every tonne of slag substituted for general Portland cement, there is a reduction of one tonne of carbon dioxide gas discharged into the atmosphere[38].

Slag recycling in the steelmaking process

An alternative approach to finding specific uses for steelmaking slag outside the steelworks is to recycle the slag inside the process itself. One of the major driving forces for this approach is the knowledge that the phosphorous content of steelmaking slag (as much as 3% P_2O_5) is usually too high for it to be returned freely to the sinter plant. At the same time, the phosphorous content is too low for the slag to be used as fertilizer. Moreover, the global supply of iron ores with low phosphorous content is diminishing and in the result, the control of phosphorous in iron and steelmaking processes has become an ever-increasing problem. In applying their minds to the challenge of finding a solution to phosphorous control, Li *et al.*[41], proposed a waste-free steelmaking process in which slag is recycled within the steelmaking process itself and a high phosphorous containing slag, suitable for use as fertilizer, is produced. Although their study was confined to a modelling exercise, the principles applied are of generic nature and their approach deserves further deliberation.

The proposed steelmaking route is shown in Figure 9: The hot-metal product from the blast furnace is de-siliconized in the De-Si furnace and de-phosphorized in the De-P furnace before refining is done in a conventional basic oxygen Converter. This part of the process is standard operating practice in many steelmaking shops. The following new concepts are introduced:

- All the slag produced in the Converter, operating at 1923K, is returned to the De-P furnace
- All the slag from the De-P furnace, operating at 1623K, is transferred to the Regenerator
- The Regenerator, operating at 1873K, contains carbon-saturated hot-metal and most of the phosphorous is transferred from the slag to the hot-metal
- The phosphorous containing hot-metal from the Regenerator is transferred to De-P-II, also containing hot-metal and operating at 1623K. Synthetic slag of high phosphate capacity is introduced into this unit and the phosphorous from the hot-metal is transferred to the synthetic slag to produce the Final Slag
- Some of the dephosphorised Regenerator slag is returned to the De-P furnace and the remainder to the De-Si furnace
- All the slag from the De-Si furnace, operating at 1623K, is returned to the blast furnace or sinter plant.

In this proposed process, slags produced in the two hot-metal pre-treatment units (De-Si and De-P), the Converter and the Regenerator are fully recycled. The only slag that exits the steelmaking process is the Final Slag from De-P-II. This slag contains more than 10%P and can be used as fertilizer.

Li *et al.*[41] conducted heat and mass balances in the proposed process and took into consideration the relevant thermochemistry in each unit process, the prevailing oxygen potentials, the appropriate activities of components in the liquid metallic phases and estimated the activities of components in molten slags. For the purposes of their analysis the Regenerator and De-P-II were operated as follows:

- For each batch of hot-metal charged from the De-P furnace to the Converter, the Converter slag is returned to the De-P furnace and the slag from the De-P furnace transferred to the Regenerator
- Some of the Regenerator slag is returned to the De-P furnace and the remainder to the De-Si furnace
- During such a cycle, the phosphorous content of the hot-metal in the Regenerator is increased and when, after a few cycles, a predetermined phosphorous level is reached, the hot-metal is poured into De-P-II, synthetic slag is added and the phosphorous transferred to the synthetic slag. The liquid hot-metal is then poured back into the Regenerator.

Li and co-workers analysed the influence of the percentage Regenerator slag that is recycled to the De-P furnace, on the mass of slag generated in each unit process; the phosphorous distribution between metal and slag; process heat requirements and the required coke supply to the *Regenerator* to keep the hot-metal saturated with carbon. They found that if up to 80% of the Regenerator slag is recycled to the De-P furnace, a steady sate is attained and optimum-operating conditions could be

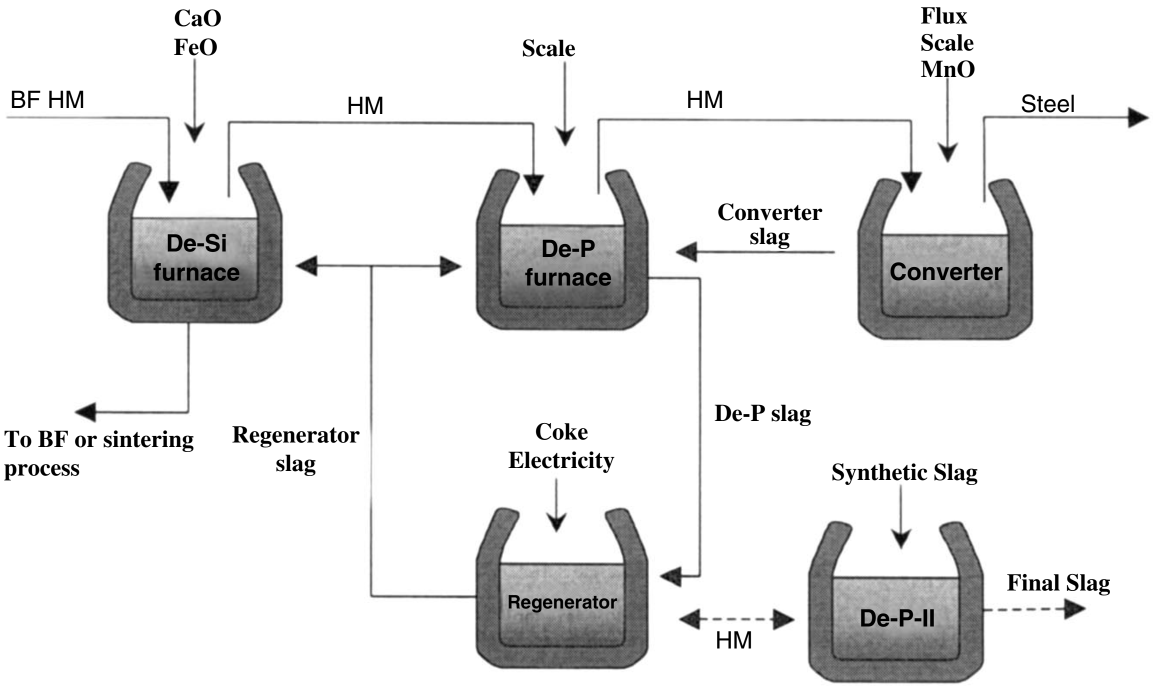

Figure 9. Proposed route to fully recycle slag in a steelmaking process[41]

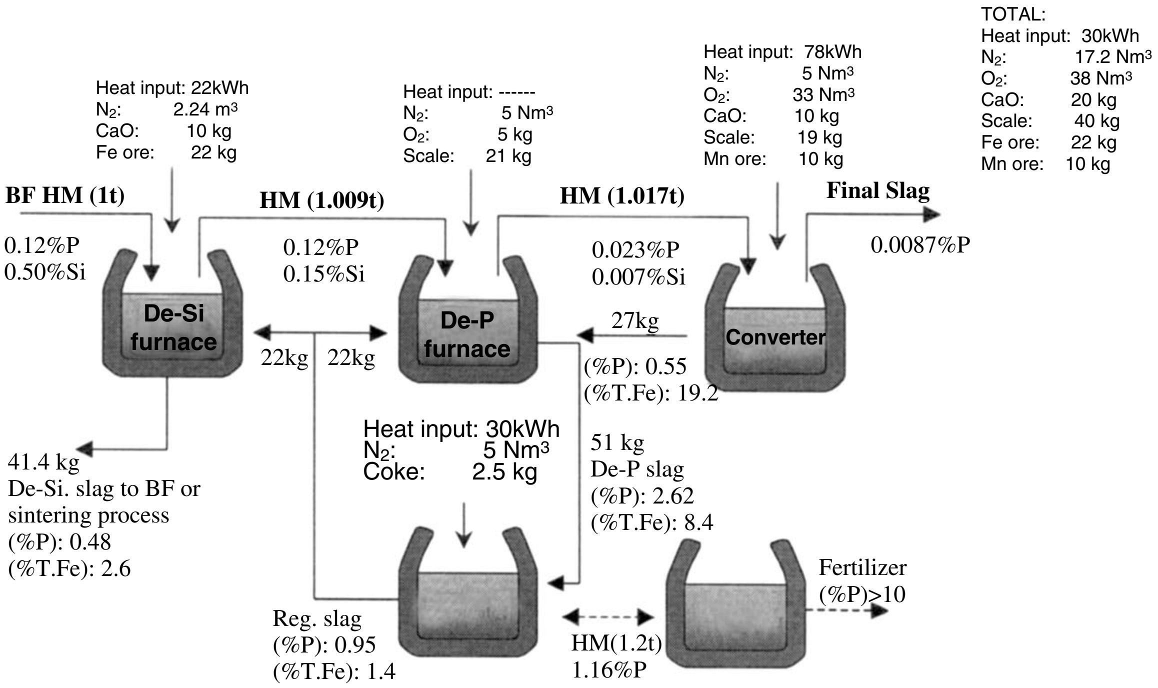

Figure 10. Heat and mass balances for the proposed route to fully recycle slag in a steelmaking process[41]

determined as a function of the analysis of the hot-metal product of the blast furnace. The optimum-recycling ratio is 50% for hot-metal containing 0.5% Si (this means that 50% of the slag produced in the Regenerator is recycled to the De-P furnace and the other 50% is transferred to the De-Si furnace)

An example of a heat and mass balance for the overall proposed process to produce high carbon-high manganese steel is given in Figure 10. In this sample calculation, the hot-metal product from the blast furnace is of the following composition: 5.04%C-0.5%Si-0.3%Mn-0.12%P. A recycling ratio of 50% was used and, hence, 22 kg of the 44 kg slag produced in the Regenerator is returned to the De-P furnace and 22 kg to the De-Si furnace. This model calculation shows that low phosphorous steel can be produced through the proposed process and that the slag generated in the individual unit processes can be fully recycled as shown. The total energy requirement is 130 kWh/t and the lime consumption is approximately one half of that of a conventional steelmaking process[41].

Conclusions

- Environmental concerns and economic realities demand that slag production in iron and steelmaking processes be reduced and that slag be effectively utilized.

- A much-improved understanding of the nature, role and function of slag has led to the optimization of the use of slags and, in current operational practice the compositions and physical properties of slags are judiciously designed to optimize the operations in the respective metallurgical reactors
- Through a better understanding of the blast furnace process we have seen a significant reduction in blast furnace slag production. Blast furnace slag is utilized in various applications but, currently, the optimum use is in the manufacture of cement
- Steel processing technology has undergone significant changes in recent years. Emphasis has been placed on the removal of silicon, sulphur and phosphorous from the hot-metal product of the blast furnace before refining in an oxygen converter or electric-arc furnace is done and on ladle metallurgy following decarburization. Commercially, converter slags are largely utilized in construction applications whereas most of the pre-treatment and ladle slags are discarded or is used in landfill applications
- Steelmaking slag, solidified by splashing liquid slag on to the walls of a BOF vessel, is effectively utilized as a consumable refractory lining
- Modelling exercises have shown that, in principle, a slag-free steelmaking process can be designed.

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