

SLAG VALORISATION SYMPOSIUM



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International Slag
Valorisation Symposium
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Leuven, Belgium

Editors

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ACKNOWLEDGEMENTS

We have thoroughly enjoyed organizing this *1st International Slag Valorisation Symposium*, bringing together approximately 100 slag specialists from all over the world. We hope that this Symposium will be the first in a long list of successful Symposia. It should also be stressed that we see this series of Symposia as complementary to the EUROSLAG Conferences which are organised by CLOOS S.A. and EUROSLAG, with the backing of the German FEhS institute.

Organising a Conference or a Symposium is always hard work. Without the unrelenting help of a multitude of people this would not have been possible. First of all we would like to thank all the invited speakers for accepting our invitation to share their research results with us and the other 80 participants of the Symposium. In the midst of a worldwide economic crisis, it was not easy for everyone to get the authorisation to speak and/or to participate in this Symposium. A special word of thanks also goes out to the Chairpersons for this Symposium, who all gladly accepted our invitation to put in extra work during the event.

This Symposium was free of charge for all participants. Obviously, this would not have been possible without financial support. We are thus extremely thankful to the Industrial Research Fund (*Industrieel Onderzoeksfonds*) of the KULeuven, which provided the organisers with a budget sufficiently large to cover all expenses. Concurrently, we are also indebted to our industrial long term partners of our Centre for High Temperature Processes and Industrial Ecology, namely ArcelorMittal Stainless Europe, Umicore and Heraeus Electro-Nite. Without their supportive attitude the organisation of this Symposium would not have been possible in these difficult economic times.

A special word of thanks goes to An Serbruyns, who developed the Symposium website and the cover design of these Proceedings. Finally, we are grateful to all people from the MTM Department (Metallurgy and Materials Engineering), including the logistics group (Katrien Baplu, Rudi Vanlaer, Danny Dekelver, Kevin Pauwels), the Chairman of the Department (Prof. Patrick Wollants), the Financial Administrator of the Department (Dirk Hoeyberghs), all other staff from the various secretariats (Regine Cieters, Mia Pierre, Aniko Lantos, Mieke Van Audenhoven, Huberte Cloosen) and all members of the THERMO Research Group.

*Peter Tom Jones
Daneel Geysen
Muxing Guo
Bart Blanpain
March 2009*

ORGANISERS

The 1st International Slag Valorisation Symposium was jointly hosted by the *Centre for High Temperature Processes and Industrial Ecology*, and the *THERMO Research Group*, which are both part of the *Department of Metallurgy and Materials Engineering* of the *KULeuven* (Belgium).



Centre for High Temperature Processes and Industrial Ecology

This Centre consists of a co-operation between the research group 'Thermodynamics for Material and Process Development' (dep. MTM) and leading materials companies, including ArcelorMittal, Umicore and Heraeus Electro-Nite.

Domains and tools

The Centre deals with the following research domains:

- Microstructural analysis of metallurgical phases
- Thermodynamic description of metallurgical systems (slag/metal/gas/matte, phase diagram optimisation)
- Development of refractory wear models and process models
- Stimulation of industrial ecology in pyrometallurgy (closing the loop, slag valorisation, process/flowsheet optimisation, material and energy efficiency, exergy analysis)

To achieve these goals, the Centre can make use of:

- Experimental techniques for evaluating refractory wear, inclusion formation and controlled slag evolution (vacuum induction furnace, tube furnaces, CSLM etc.)
- Characterisation methods, including OM, microprobe (EDS/WDS), SEM, FIB, e-SEM, MS, Q-XRD, XRF, XPS, AAS, ICP-AES etc.
- Software programs (including FactSage, Dictra, HSC etc.)

Broad network

Apart from its three core partners (ArcelorMittal Stainless, Umicore, Heraeus Electro-Nite) the Centre has run and/or currently runs projects with a number of leading companies in the metallurgical field: ArcelorMittal Ghent, Campine, Metallo-Chimique, Nedstaal, Ascometal, RHI, Thermphos, Rockwool, Corus Steel, Rio Tinto Minerals, Posco Steel, Baosteel etc. Apart from these industrial partners the Centre has also

established a broad international research network, including FEhS, UCL, Queensland, RMIT, Carnegie-Mellon, Harvard, Pohang U. Science and Technology, McGill, USTB, University of Tokyo etc.

Projects

Two types of research projects are performed. Specific projects include short, targeted research projects, feasibility studies, definition and writing of research proposals to outside sponsors. The second type of projects consists of generic work. Generic projects are intended to strengthen the scientific and technical expertise of the Centre.

Join the Centre?

Through the partnership with an academic group, the metallurgical industry is continuously exposed to new ideas, bright students and young researchers. The Centre provides access to top level experimental, modeling and characterization facilities and thus allows a higher base level of relevant expertise and acts as a flywheel for larger industrial projects that may be government sponsored. The Centre is open for new members.

For more information, contact Prof. Bart Blanpain (bart.blanpain@mtm.kuleuven.be) or Dr. Peter Tom Jones (peter.jones@mtm.kuleuven.be) or visit the website: www.mtm.kuleuven.be/Research/centre/index.html

Part of SMaRT-PRO²

The Centre is part of a recently established KULeuven Industrial Research Fund Knowledge Platform. SMaRT-PRO² (Sustainable Materialization of Residues from Thermal Processes into Products) brings together research groups within the K.U.Leuven Association to collaborate on the valorization of inorganic byproducts, such as solid waste (including metallurgical slags) and carbon dioxide, from industrial processes. Working closely with industry, government and civil society, the generic goal is to strengthen knowledge on valorisation of inorganic industrial by-products and provide a formal platform that can enhance the closing of industrial material cycles in Flanders and abroad Platform. See: www.smartpro2.eu





THERMO Research Group

The THERMO Group, which stands for Thermodynamics in Materials Engineering, has the following scope. Thermodynamic analysis relates to the equilibrium state of materials and materials systems to macroscopic variables such as pressure, temperature, composition and stress. Combined with experimental observations of phases and the measurement of their composition, it creates the framework to understand materials and processes and presents opportunities to improve materials properties and processes used in materials production. Materials and processes, however, are seldom in a state of equilibrium. It is therefore essential to also study phenomena such as reactions, diffusion, segregation and solidification that bridge the gap between equilibrium and non-equilibrium states. It is in this broad domain that the THERMO group is active with theoretical and experimental research in both basic and applied subjects.

Research Fields

The THERMO Group deals with the following research domains:

- Pyrometallurgy
- Determination and optimisation of phase diagrams
- Modelling of microstructure evolution

For more information, contact Prof. Bart Blanpain (bart.blanpain@mtm.kuleuven.be) or Prof. Patrick Wollants (patrick.wollants@mtm.kuleuven.be) or visit the website:

<http://www.mtm.kuleuven.be/Research/THERMO/index.php>

Session 1

Mineral carbonation and CCS

Steel and CO₂ – the ULCOS Program, CCS and Mineral Carbonation using Steelmaking Slag

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Abstract

Over the past 40 years the European steel industry has reduced its CO₂ emissions with approximately 50 to 60%: this is the highest level of energy conservation achieved by any industrial sector. This is due to several decades of cost management, as high energy prices have driven the industry to optimise its processes as close as possible to physical (thermodynamic) limits. Cutting CO₂ emissions further, to the level that post-Kyoto policies require, raises therefore specific challenges: it is indeed necessary to uncouple energy savings and CO₂ reduction in the Steel sector. There is no simple process, available off-the-shelf, that can accomplish this. Deep paradigm shifts in the way steel is produced have to be imagined and the corresponding breakthrough technology designed and developed. The largest R&D program, called ULCOS (Ultra Low CO₂ Steelmaking) has been running in the EU since 2004 to progress in this direction. The present paper gives the current status of the various ULCOS options. In particular, attention is drawn to the use of CCS and mineral carbonation within new ULCOS technologies. Geological CCS has been identified from the start as a powerful solution. Mineral carbonation has also been assessed, showing that it can only result in moderate overall emissions reductions. Therefore, mineral carbonation, in particular, needs more detailed elaboration before it can be considered as an option compared to geological CCS.

Introduction

Steel is among the major structural materials in the world, with its production coming second only to that of cement. Iron and steel have been used for several thousands of years, either to make artifacts, from buildings to automobiles and from guns to cans, but also tools and machines from which all other artifacts are made. Steel is ubiquitous. The history of mankind is completely interwoven with that material. Behind the name of steel hide several thousands of different alloys, the largest family of materials ever. The Steel industry, which produces steel, is a sophisticated, modern and capital intensive industry. It features some of the most impressive engineering reactors, such as the blast furnace, which is unique and probably as powerful and complex as a nuclear reactor or a large rocket used to raise heavy payloads to orbit.

Steel production in 2007 amounted to 1.342 Gton and in 2008 to 1.3297 Gton. Anthropogenic emissions of GHGs, which amounted to 49 Gton of CO₂ equivalent worldwide in 2004,¹⁾ are traditionally split among economic sectors, among which industry represented 19.4%. The Steel Industry represents 6 to 7% of global anthropogenic CO₂ emissions according to the IPCC,¹⁾ but only 4-5% according to the IEA,²⁾ *i.e.* one fourth to one third of the whole industry sector. These estimates include direct emissions by the steel mills themselves and indirect ones, generated by the energy sector to produce the electricity that the mills consume. This accounting method leaves out a life-cycle presentation, where the benefits of using steel, in terms of CO₂ emissions that can be allocated to using it, would be taken on board: this would account for avoided emissions at least an order of magnitude larger than the emissions of the steel mills. But in a traditional analysis, this scenario modeling of a society that uses steel, against an hypothetical one that would not, is usually not considered.

The carbon dioxide intensity of the steel sector today is 1.9 t_{CO2}/t_{crude steel}. The Steel Industry comes out as a small emitter compared to the energy sector (25.9%), transport (13.1%), forestry (17.4%) or agriculture (13.5%). However, the CO₂ stream is generated by a relatively small number of large emitters, each one spouting out between 1 and 10 Mton per year.

CO₂ emissions of the Steel Sector

Why does the Steel Industry generate CO₂? There are two main reasons: on the one hand, energy is needed to produce steel, more often than not generated from fossil fuels, while on the other hand, reducing agents are necessary to produce steel from iron ores, the cheapest, most easily available reductant being the carbon of coal. Figure 1 shows the various production routes used today to make steel and their share in the world and in France. The Blast Furnace (BF) route produces steel from primary raw materials, *i.e.* iron ore and requires both energy and reducing agents in the form of coke and pulverised coal; it is called an Integrated Steel Mill. The Electric Arc Furnace (EAF) route produces steel from secondary raw materials, *i.e.* iron scrap, and needs mainly energy, in the form of electricity, along with some coal and oxygen. The DR route is based on ore and uses natural gas as the reducing agent and fuel, along with electricity for subsequent processing in an EAF. The carbon dioxide intensity of the three routes is respectively 1.97, 1.10 and 0.45 t_{CO2}/t_{crude steel}.

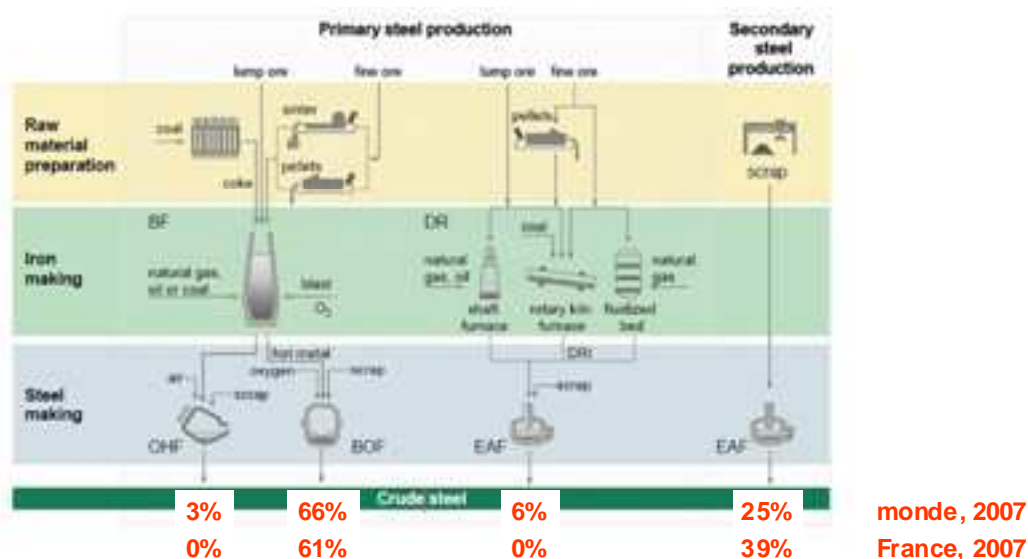


Figure 1: Production routes to make steel today, with production shares in the world and in France (BF: Blast Furnace; OHF: Open Hearth Furnace; BOF: Basic Oxygen Furnace; EAF: Electric Arc Furnace; DR: Direct Reduction)

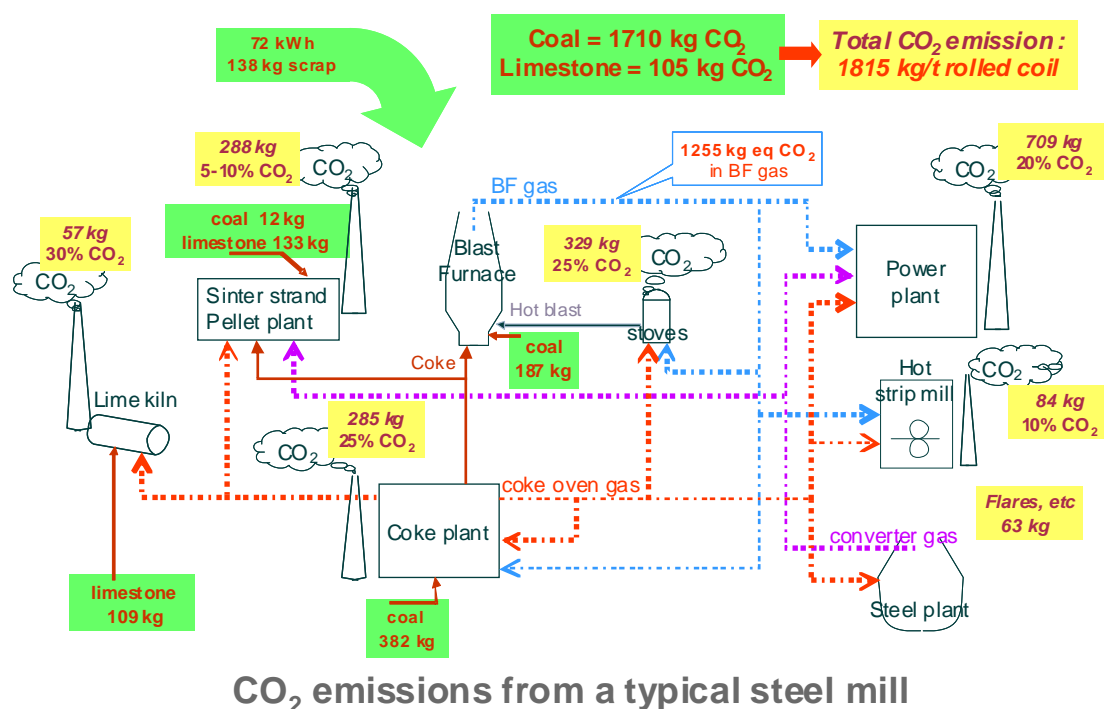


Figure 2: Simplified flow sheet of an Integrated Steel Mill, showing carbon-bearing material input (green boxes, highlighted), CO₂ emissions, expressed in volume (kg/t of hot rolled coil) and concentration in the flue gas (volume %).

An Integrated Steel Mill (ISM) is a complex series of interconnected plants, where CO₂ comes out from many stacks (10 or more). Figure 2 gives a simplified carbon balance, showing the major entry sources (coal and limestone) and the stack emissions, in

volume (kg/t of hot rolled coil) and concentration of CO₂ (volume %). The major CO₂ stream comes out of the blast furnace and accounts for 69% of all Steel Mill emissions to the atmosphere. This is indeed where most of the reduction takes place and where most of the energy is needed. The top gas of the blast furnace is composed of roughly 25% of CO₂, the rest being CO at a similar concentration with a complement of nitrogen. The other stacks all together account for 31% of the emissions: they exhibit rather low CO₂ concentrations, typical of the flue gas in a conventional boiler, combustion chamber or power station. Of course, the BF top gas never ends up directly in a stack, as the embedded energy is recovered in a power plant, which is part of the Mill complex. A Direct Reduction steel mill generates CO₂ in lesser quantities at the stack of the DR plant - as well as downstream at the steel shop and rolling mills, like in the ISM. An EAF mill generates even smaller amounts of CO₂, from the steelshop on: most of its emissions are actually due to electricity production needed to power the EAF.

Strategies to control CO₂ emissions from the Steel Sector

A state of the art Steel Mill is a very optimised system in terms of consumption of fuels and reducing agents. The Blast Furnace itself operates 5% away from thermodynamic limits and the whole mill has a potential of energy savings of roughly 10% only. This is due to several decades of cost management, as high energy prices have driven the industry to optimise its processes as close as possible to physical limits. The Industry rightfully claims energy savings and, correspondingly, CO₂ cuts which range between 50 and 60% over the last 40 years, depending on the local conditions: this is the highest level of energy conservation achieved by any industrial sector. Cutting CO₂ emissions further, to the level that post-Kyoto policies require, raises therefore specific challenges: it is indeed necessary to uncouple energy savings and CO₂ reduction in the Steel sector – an original feature compared to other sectors.

First, a more or less obvious fact that ought to be stated anyway, is that the usage of steel scrap should be kept at the high level that it has reached today. It is estimated that the collecting rate of obsolete scrap is around 85% today, which forms the basis of a strong recycling economy, complete with scrap dealerships and a specific steel production route based on the EAF. In simple words, value is created by the recycling of virtually all available scrap. In the long term, this situation will continue. It should also be pointed out that the indirect emissions related to electricity production will evolve with time. For example, ULCOS has shown that, under a strong carbon constraint, the carbon intensity of the European electricity grid will drop from 370 g_{CO2}/kWh in 2006, to 144 g in 2050, a specific drop of 55% which will be translated at the same level in indirect emissions.³⁾

The major source of CO₂ emissions from steel mills still remains the ore-based route, which will retain an important role in the long term, at least until a recycling society can replace the 20th and 21st century economy of production growth that is mainly driven by population growth – probably some time in the next century or at the very end of the present one.

Solutions to curtail emissions from the ore-based route have to be exhibited and it is clear from the previous sections that there is no simple process, available off-the-shelf, that can accomplish this. Deep paradigm shifts in the way steel is produced have to be imagined and the corresponding breakthrough technology designed and developed, by strong R&D programs. The largest such program called ULCOS, for Ultra Low CO₂ Steelmaking, has been running in the EU since 2004 to progress in this direction.^{3,4)} The analysis that ULCOS has proposed in terms of Breakthrough Technologies is shown in Figure 3, which explains how reducing agents and fuels have to be selected from three possibilities: carbon, hydrogen and electrons, mostly in the form of electricity.

The present steel production technology is based on coal, *i.e.* mostly on carbon, on natural gas, a mix of carbon and hydrogen and on electric arc furnaces. To identify CO₂-lean process routes, 3 major solution paths stand out and three only: either (1) a shift away from coal, called decarbonising, whereby carbon would be replaced by hydrogen or electricity, in processes such as hydrogen reduction or electrolysis of iron ore, or (2) the introduction of CCS technology, or (3) the use of sustainable biomass.

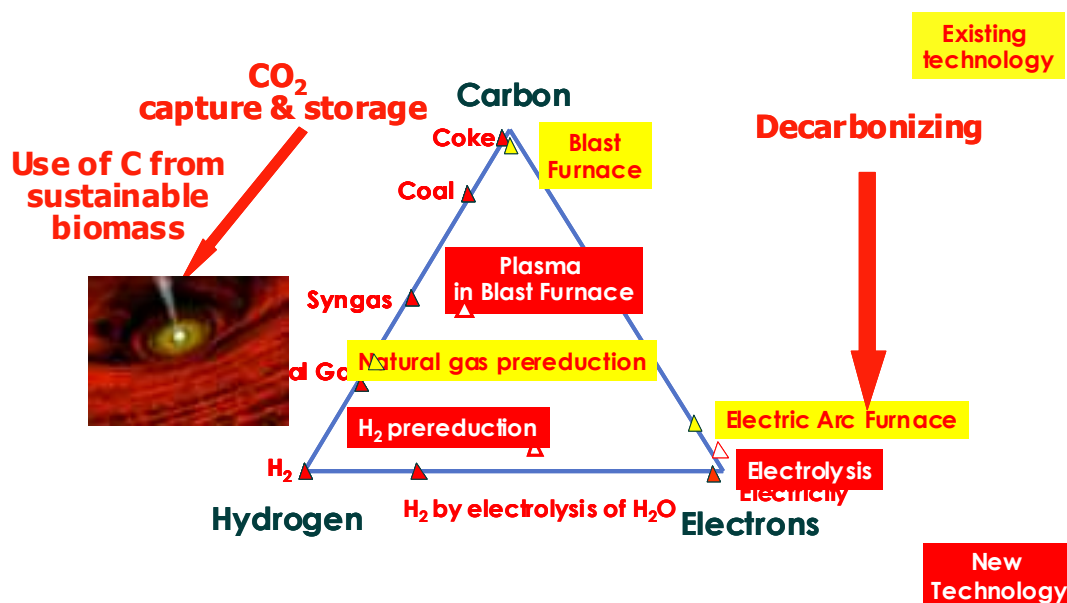


Figure 3: Pathways to breakthrough technologies for cutting CO₂ emissions from the ore-based steel production routes

ULCOS has investigated about 80 different variants of these concept routes in the initial phase of its research program, using modeling and laboratory approaches to evaluate their potential, in terms of CO₂ emissions, energy consumption, operating cost of making steel and sustainability.^{3,4)} Among all of these, six broad families of process routes have been selected within the ULCOS program for further investigation and eventual scale up to a size where commercial implementation can take over:

- a *blast furnace* variant, where the top gas of the Blast Furnace goes through CO₂ capture and the remaining reducing gas is reinjected at the base of the reactor, which is moreover operated with pure oxygen rather than hot blast (air). This has been called the Top Gas Recycling Blast Furnace (TGR-BF). The CO₂-rich gas stream is sent to storage (Figure 4);
- a *smelting reduction process* based on the combination of a hot cyclone and of a bath smelter called HIsarna and incorporating some of the technology of the HIs melt process.⁵⁾ The process also uses pure oxygen and generates off-gas which is almost ready for storage (Figure 5);
- a *direct reduction process*, called ULCORED, which produces DRI in a shaft furnace, either from natural gas or from coal gasification. Off-gas from the shaft is recycled into the process after CO₂ has been captured, which leaves the DR plant in a concentrated stream and goes to storage (Figure 6);
- two *electrolysis variants*, ULCOWIN and ULCOLYSIS, which respectively operate slightly above 100°C in a water alkaline solution populated by small grains of ore (electrowinning process), or at steelmaking temperature with a molten salt electrolyte made of a slag (pyroelectrolysis);
- two more options are available: one consists in using *hydrogen for direct reduction*, when and if it is available without any carbon footprint; the other is based on the use of *sustainable biomass*, the first embodiment of which is charcoal produced from sustainable eucalyptus plantations grown in tropical countries.



Figure 4: Schematics of the TGR-BF process

In the nearer term, the TGR-BF seems the most promising solution, as existing Blast Furnaces can be retrofitted to the new technology and thus extensive capital expenditures that would be necessary to switch over to the Breakthrough Technologies are maintained under some control. Moreover, the very principle of the process delivers energy savings because the capture of CO₂ and the recycling of the purified gas displaces high temperature chemical equilibria (Boudouard reaction) and uses coke and coal with a higher efficiency inside the BF than is possible with conventional operation. This balances the extra costs incurred by the capture and storage, to some extent. The concept has in addition been tested on a large scale laboratory blast furnace in Luleå, with a positive outcome.

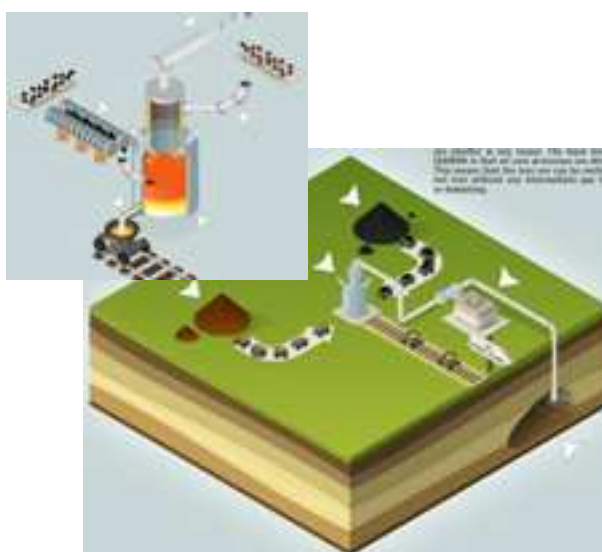


Figure 5: Schematics of the HIsarna process

Where natural gas is available, ULCORED is an attractive option. A 1 t/h pilot is planned to be erected in Luleå in the next few years by LKAB, an ULCOS partner, to fully validate the concept. Somewhat later and probably for greenfield steel mills, the HIsarna process will also be an option. An 8 t/h pilot is to be erected and tested in the course of the ULCOS program. The electrolysis processes have been developed from scratch within the ULCOS program and, therefore, are still operating at laboratory scale. Although they hold the promise of zero emissions, if they have access to green electricity, time is required to scale them up to a commercial size (10 to 20 years).

Hydrogen steelmaking will depend heavily on the availability of green hydrogen, while the use of charcoal, far way from growing countries, would require the set up of complex logistics, including heavy infrastructure across several continents. The discussions have been centered until now on the major sources of CO₂, which allows to cut emissions for the whole steel mill by more than 50%. It is possible to cut emissions

further, by treating the other stacks of the steel mill: the cost of abatement would of course be higher. With this rationale, though, zero emissions could be achieved.

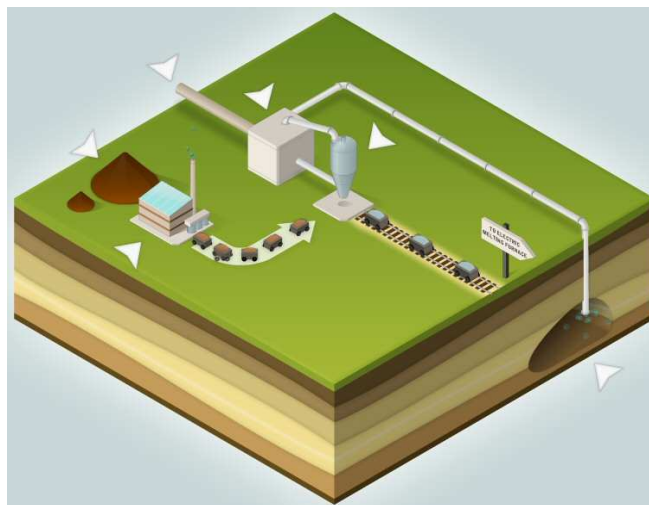


Figure 6: Schematics of the ULCORED process

In parallel to ULCOS, other programs have been launched under the umbrella of the worldsteel CO₂ Breakthrough Program.⁶⁾ Their rationale is similar to the one of ULCOS. They are less advanced in terms of making Breakthrough Technologies available. This long development on Breakthrough Technologies shows that there is no simple recipe for cutting the present CO₂ emissions of the Steel Industry by 50% or more (the objective of the ULCOS program): new technologies have to be developed, which means a high level of risk, incompressible development time, large budgets for R&D and then large capital expenditures to convert steel mills to the Breakthrough processes. Moreover, the economic viability of these solutions, which definitely are not no-regret, will depend on the price of CO₂ and on the implementation of a level playing field for climate policies all around the world that avoid “carbon-havens” and therefore carbon leakage, especially out of Europe. With all these caveats, the Steel Industry can cut its emissions significantly and continue to provide a material that the world needs to ensure a good life to its citizens and cut CO₂ emissions in other sectors.

CCS for the Steel Sector

This section will refocus on CCS for the Steel sector, because implementing CCS seems to be the quickest way – in the 2020s – to delivering significant cuts in the CO₂ emissions of the sector. The first point is that CCS will be implemented in the Steel Industry without matching any of the existing CCS categories, which have been defined with the context of energy generation in mind. Indeed, in the Steel sector, the major part of the generation of CO₂ is related to the reduction of the iron oxides that constitute iron ore. Oxyfuel combustion, pre- or post-combustion capture chemical looping do not

mean much in an industrial context where there is no combustion and no oxidation either – except very locally inside the reactors. Figure 7 presents the various CCS concepts applied to the steel industry and to a combustion process.

The proper concept to apply to the TGR-BF is that of *in-process CO₂ capture, with oxygen operation*. The oxygen part is similar, but not identical to oxyfuel operation. The recycling part is original and is the key reason why some energy savings and the corresponding cut in operating cost are gained. The same concept applies to the ULCORED process, which also includes the use of pure oxygen and in-process recycling of the shaft top-gas, in addition to other features like a series of shift reactors in the recycling loop.

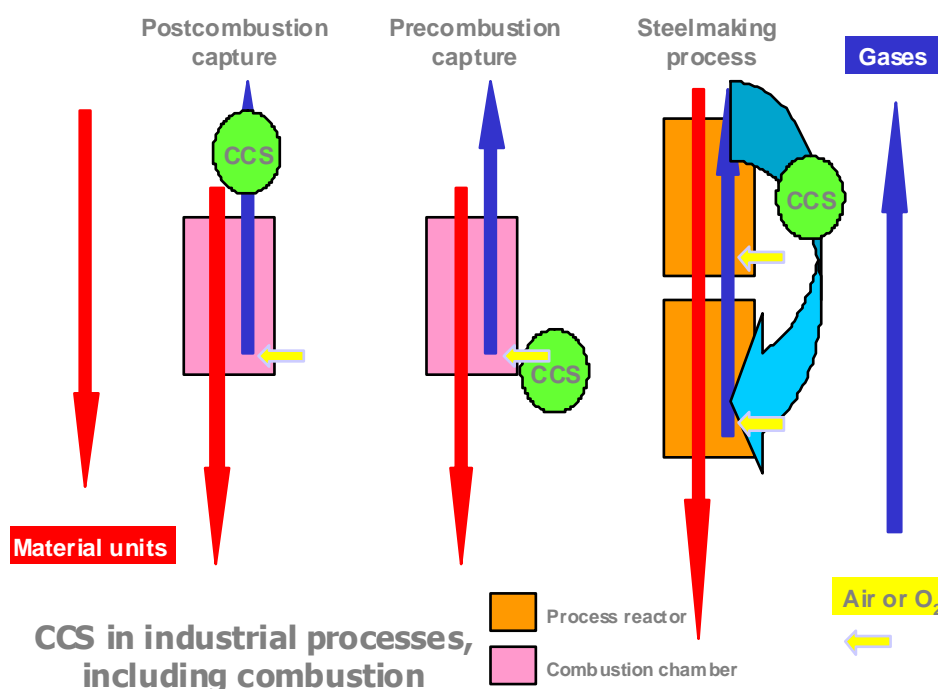
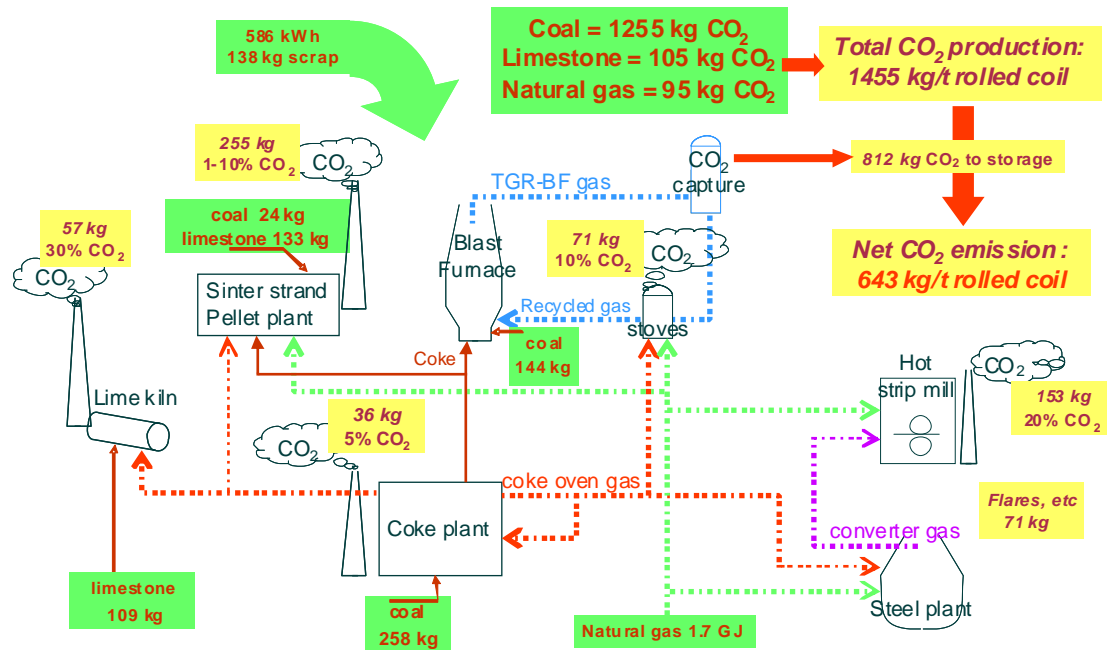


Figure 7: Implementation of CCS in process industries including combustion

The HIsarna process is slightly different from the two other processes as it does not involve a recycling loop for the gas: the smelter gas is oxidised at the cyclone level, where some reduction is carried out along with combustion to preheat and melt the ore. There is a counter current flow of the gas against the iron stream, in which its chemical energy is fully exhausted.

Figure 8 shows the carbon and CO₂ mass balances of a steel mill operating with TGR-BF. Emissions are cut by 65% compared to the non-ULCOS benchmark steel mill of Figure 2 (and by 56% in the steel mill itself, due to the carbon saving introduced by the process). Capturing the flue gas of an extra stack, like that of the sinter plant, would

bring the reduction at the level of 75%. The most striking feature of the top gas stream from which CO₂ is recovered is the high concentration of CO₂, around 35%, which is significantly more than in the top gas of the conventional blast furnace.



CO₂ emissions from a TGR-BF steel mill

Figure 8: Simplified flow sheet of an Integrated Steel Mill operating with a TGR-BF, showing carbon-bearing material input (green, highlighted boxes), CO₂ emissions, expressed in volume (kg/t of hot rolled coil) and concentration in the flue gas (%).

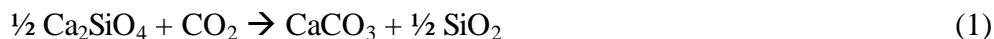
CO₂ storage for the steel sector

Storage of CO₂ can take place in geological reservoirs (geostorage), in the ocean or by the mineralisation of some other compounds, chemical reactants or rocks (*ex situ* storage). In the context of the present Symposium, we now focus on mineral sequestration (mineral carbonation).

Mineral sequestration

Mineral sequestration is an option which has been seriously examined in the ULCOS program (for example in ref.⁷⁾) and also by the World Steel Association. The concept is simple: some minerals such as magnesium-rich ultramafic rocks (peridotites, serpentines, gabbros, *etc.*) can react spontaneously (negative enthalpy of reaction) with CO₂ and form carbonates, which stand below CO₂ on the oxido-reduction scale:⁸⁾ the compounds are usually stable and the only difficulty of these schemes is to master the kinetics of reactions, which naturally take place in the realm of geology, with the corresponding time scales. Some of the reactions may involve lime or magnesia and bicarbonates may also be formed. A scheme specific to the steel industry proposes to

use slag, especially steelmaking BOF slag, as the reactant that will be used to absorb CO₂ by a chemical reaction: there is a phase in that slag, called larnite (Ca₂SiO₄) and present at the level of 30 to 40%, which can react with CO₂:



with an enthalpy of - 22 kcal. In addition to larnite, slag may contain as much as 6% free lime (CaO), which also reacts with CO₂ to form the same calcium carbonate. The use of slag has been studied in the ULCOS program,⁷⁾ where it was shown that the reaction can proceed at moderate temperatures (90°C), high pressures (100 bar), and moderate times of reaction (90 min) if the slag is ground (50 µm) to liberate the calcium silicate, mixed with water to produce a slurry and kept agitated during the reaction process. 70% of carbonation is achievable under these conditions, which means that 1 ton of slag can capture 250 kg of CO₂.

Comparing this amount of stored CO₂ with the Steel Mill emissions and the amount of slag which is generated in parallel, shows that only 1.3% of the total CO₂ generated by the Steel Mill (0.1 CO₂ Mt compared to total emissions of 7.2 Mt/y) can be sequestered in this way. The ULCOS program conclusion was that this was not measuring up to the level of the challenge and did not match in any way the 50% mitigation target that was its goal.

Now, if mineral carbonation was to provide more sequestration, then more reactant would have to be used, roughly 100 times more. This shows the level of the logistics involved, as it would amount to 25 times the mass of steel produced. Proponents of mineral carbonation do not suggest to move the rocks to the Steel Mill, but rather the gas to the mine. This, however, is a proposal that needs more detailed elaboration before it can be considered as an option compared to geostorage. (*See also other contributions on mineral carbonation in these Proceedings, which focus on improved, accelerated carbonation.*)

Conclusions

The Steel Industry has been aware of the Climate Change threat since the late 1980s and started to propose solutions early.⁹⁾ CCS has been identified from the start as a powerful solution to deal with this issue. Cooperative programs have been launched in Europe and in the rest of the world to tackle the issue at various scales and commercial-size demonstrator experiments are now under way, which may lead to implementation and deployment from the 2020s onwards. This is a long term agenda, full of promises but also of risks and traps, a situation which is probably similar to what other sectors are experiencing. Risks are related to the complexity of the issue, which calls on the

development and the implementation of breakthrough technologies under time constraints which are very short. The message is not that CCS is unlikely to happen in the Steel Industry, quite the opposite. But we believe that the optimism which prevails in many policy-driven publications is overrated. Some researchers are actually becoming aware of this situation.¹⁰⁾

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Mineral Carbonation at K.U.Leuven: a review

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Abstract

For more than 20 years, K.U.Leuven has contributed to international mineral carbonation research. Investigated materials include lime mortars, hydraulic mortars, alkaline wastes and hydrated waste-cement blends. Attention was given to processing conditions, product properties (structural, mineralogical and environmental) and *in-situ* analysis. In particular, results were achieved on the relation between CO₂ diffusion and water content in the material, on the identification of different reaction stages, on the industrial applicability of in-line carbonation, and on the microstructural and chemical speciation of reacted phases. In the future, the focus areas will be further explored in a more collaborative effort.

Introduction

Research relative to carbonation of solid materials started at K.U.Leuven in the late eighties of the previous century. At that moment Koen Van Balen started to investigate the carbonation reaction mechanism in lime mortars and the effects on historical buildings. The carbonation reaction of calcium hydroxide (lime) in mortars is crucial from an engineering point of view, as it is the primary or the secondary hardening reaction, depending on the binder composition, that improves the mechanical properties and therefore structural behaviour of the masonry. Specification of lime mortar properties is essential to understand how it affects the overall durability and deformability of the historic masonry. In particular, the focus was directed on modelling the carbonation process and the influence of the water content on the reaction progress. Later on, his group widened the focus to include various building materials besides lime mortar such as lime hydrate and hydraulic binders (cements). Also the relation and competition between carbonation and hydration in hardening processes were and are studied. A dedicated set-up was designed for this research including *in-situ* XRD analysis of the carbonated material, which allows following the progress of the carbonation reaction in detail. A close collaboration exists with the mineralogy group of Jan Elsen. Meanwhile another group, including Tom Van Gerven and Carlo Vandecasteele, started to be interested in carbonation from the waste treatment point of view. As carbonation is considered to be one of the main reactions taking place in

weathering solid wastes, it was necessary to take this process into account when assessing long-term treatment options. The effect of carbonation on leaching of heavy metals from incinerator residues became a focal point of the group, both with respect to solid waste as such and solid waste incorporated in cement matrices. When it became clear that in some conditions, carbonation can have a positive effect on heavy metal leaching (*i.e.* decrease leaching), accelerated carbonation was investigated as a treatment method to enhance environmental properties.

Over 20 years of investigation has led to various papers, conference communications and PhD dissertations in the field of carbonation. A list of the most important ones is provided in the references.¹⁻²⁶⁾ In the future the groups will collaborate to investigate mineral carbonation systematically, with a focus on processing conditions, product properties (structural, mineralogical and environmental) and *in-situ* analysis.

This conference paper reviews the most important findings at the K.U.Leuven relative to mineral carbonation, by focusing on the three domains of expertise: processing conditions, product properties and *in-situ* analysis. At the end, future directions of the research are described.

Contributions by K.U.Leuven

The carbonation reaction in mortars and other alkaline materials is a rather complex mechanism composed of diffusion of the CO₂ through the pore structure and its dissolution in the capillary pore water where its reaction with calcium hydroxide occurs with the precipitation of calcium carbonate crystals. For a better understanding of this reaction mechanism in mortars, research has been carried out to clarify the diffusion term and the reaction term. Based on gas diffusion in a porous medium, Van Balen¹⁾ provided the very first one-dimensional modelling of the lime mortar carbonation, taking into account the combined CO₂ diffusion with water (vapour) transfer. This research has identified the interrelationship between CO₂ diffusion and water content in the mortar, considering the water produced from the carbonation reaction itself. Numerical models show that the carbonation reaction starts quickly on the outer surface of the lime mortar and the CO₂ diffusion controlled phase starts when the mortar has dried enough. The quick start and fast blockage is due to the limited diffusion resistance at start and due to the blockage of diffusion resulting from the water produced by carbonation.^{1,2)}

The carbonation reaction model in lime mortars was improved with further research based on experimental studies on the diffusion term and the reaction term. The effective diffusivity of CO₂ in carbonated lime mortars was studied using a Wicke and Kallenbach type of set-up composed of a diffusion cell and a CO₂-gas analyzer.³⁾ The CO₂ diffusion coefficient was determined in relation to different water contents.

Experimental results have indicated that the CO₂ diffusion coefficient decreases almost linearly when increasing the water content from a dry mortar to capillary saturation due to the blockage of the CO₂ diffusion by water (Figure 1). Due to the presence of coarse pores in lime mortars, the influence of water content on CO₂ diffusivity is much less pronounced than in cement mortars composed of sorption pores. Therefore, CO₂ diffusion in lime mortars can take place at high moisture contents and it is only blocked at a water content above saturation by capillary suction. This particular property of lime mortars allows the water vapour transport inside a masonry wall and therefore contributes to the durability of the masonry.

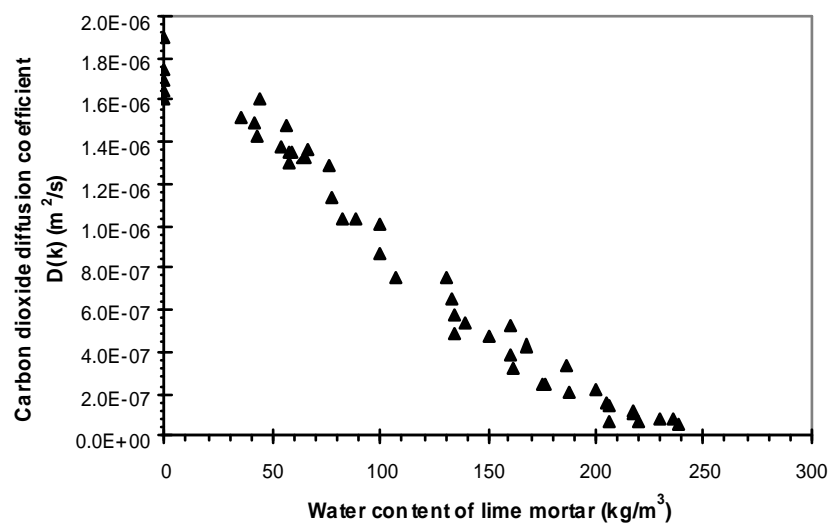


Figure 1: Influence of water content on the CO₂ diffusion coefficient of a lime mortar.

In the case of incinerator bottom ash samples, moisture content also influences carbonation rate and subsequent metal leaching.⁸⁾ For the particular material, a moisture content range of 13-25% minimised leaching of copper, chromium, molybdenum and antimony. Keeping the moisture content constant during carbonation requires, however, tight control of processing conditions. During carbonation experiments of incinerator bottom ash in the lab, the moisture content of the samples decreased to 6% within 75 hours of treatment in a CO₂ chamber with > 95% relative humidity in the atmosphere, regardless of the original moisture level (up to 50%). On the other hand, when the same type of samples was carbonated in the stack gas of a municipal solid waste incinerator, containing approximately 10% CO₂ and 21% of water vapour, the ash-filled column flooded because of water condensation due to the temperature decrease in the stack by-pass from approximately 112°C to 10-20°C.¹³⁾ This unwanted effect can easily be avoided by condensating part of the water vapour prior to carbonation. Although flooding of the column complicated interpretation, it could be concluded that stack gas carbonation yields the same results in terms of pH decrease and metal leaching as those

obtained from pure CO₂/N₂ gas mixtures in the laboratory. Direct in-line mineral carbonation thus seems to have potential.

Related to the industrial application of in-line ash carbonation, the concept of leading the stack gas in counter-current over a layer of bottom ash on a moving belt has been investigated with respect to the acceptable thickness of the bottom ash layer.¹³⁾ Figure 2 gives the pH results over time for a 10 cm thick layer of bottom ash of which the top surface was contacted with 10% CO₂ at 50°C. After one week almost the complete sample had reached pH 8.5-9 and was considered to be carbonated. A simple model predicts the experimental results reasonably well. Further process improvement is obviously necessary before industrial feasibility can be considered.

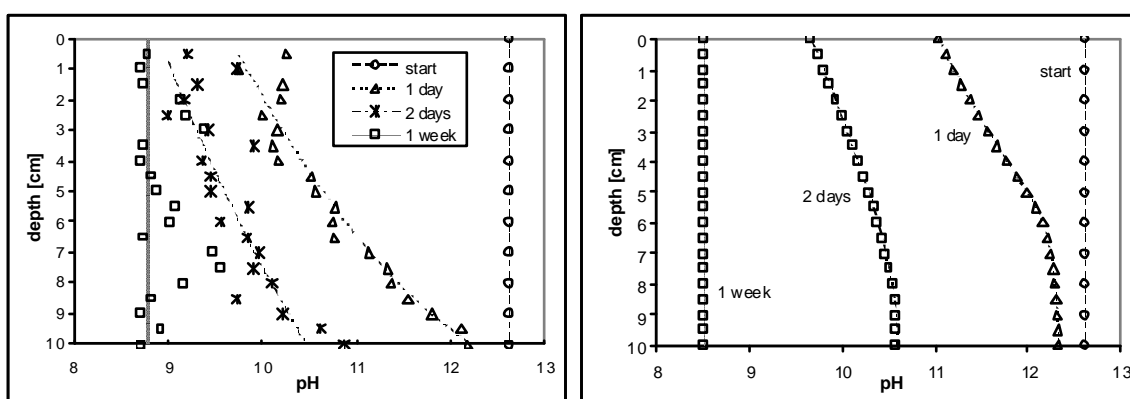


Figure 2: Experimental (left) and modelling (right) results of accelerated carbonation of a 10 cm bottom ash layer over time.

The reaction term was studied using a carbonation experimental set-up that was developed at the department of Civil Engineering. In this set-up, lime paste is subjected to high CO₂ concentration to simulate an accelerated carbonation process. This experimental study is based on measuring the CO₂ concentration during the carbonation reaction. Net CO₂ uptake by calcium hydroxide is determined and based on this the reaction rate is calculated. Using this set-up, the carbonation reaction was studied at ambient temperatures with various lime binders⁷⁾ and with hydraulic binders²⁴⁾ at various CO₂ gas concentrations (20%, 50% and 100%). This study has verified the lime mortar carbonation model and has improved understanding of the factors influencing the carbonation reaction rate in a porous system. The reaction rate is not proportional to the CO₂ gas concentration but is rather influenced by the material properties of lime as the specific surface area. In the case of incinerator bottom ash, there is also no advantage in increasing the CO₂ gas concentration, which again illustrates that a 10% CO₂ stack gas is very suitable for mineral carbonation processes.^{8,13)}

Further insights have been gained on the carbonation reaction mechanism and on the reaction rate with recent research using this carbonation experimental set-up coupled

with an in-situ XRD analysis.¹⁹⁾ This coupled set-up allows following the real-time modification of the mineral phases of portlandite and calcium carbonate while measuring the CO₂ uptake simultaneously. The carbonation reaction rate obtained from CO₂ uptake and that obtained from calcite precipitation are compared. The results have revealed that the carbonation reaction proceeds in two phases: (I) initial CO₂ uptake by the sample surface; (II) increased CO₂ uptake leading to the acceleration of the reaction (Figure 3). During the first phase, CO₂ molecules are rapidly absorbed by the alkaline water on the surface. This triggers the carbonation reaction with the precipitation of calcite crystals (Figure 4). While the CO₂ uptake continues at a decreasing rate, the calcite precipitation does not follow the same rate. This indicates that a dormant period exists in which the reaction controlling factors are the rates of CO₂ absorption and of calcium hydroxide dissolution in water. The second phase when CO₂ uptake increases, starts after the sample has dried enough. This creates open pore space, facilitating CO₂ diffusion through the sample thickness and accelerating the carbonation reaction resulting in a complete carbonation of the surface.

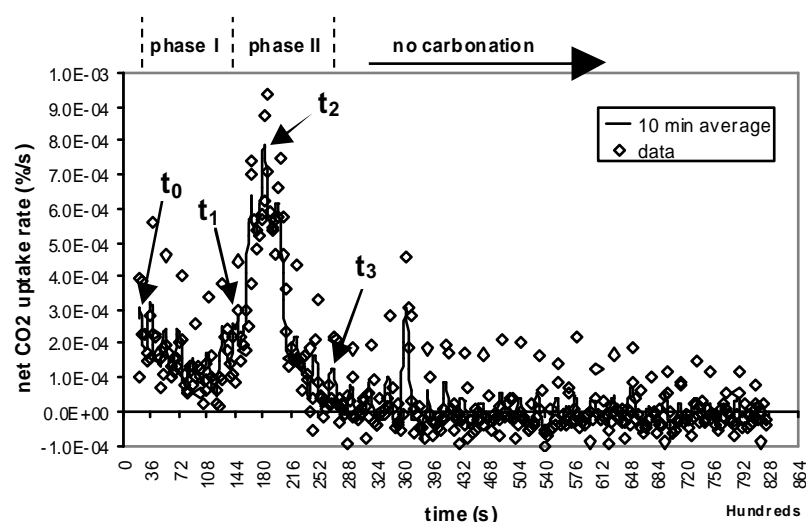


Figure 3: CO₂ uptake rate of a lime paste (t_0 : start of reaction; t_1 : start of increased CO₂ uptake; t_2 : time of maximum CO₂ uptake rate; t_3 : end of reaction).

Product properties have also been investigated, with specific attention to microstructural evaluation and effects on metal leaching. Microstructural investigation of the carbonated profiles formed under different conditions has indicated that calcite is the only calcium carbonate polymorph precipitating and that its precipitation rate is independent from the CO₂ concentration, relative humidity conditions and physical properties of the lime particles.²⁴⁾ These three parameters, however, have an important impact on the habit, size and morphology of the precipitated calcite. In particular, CO₂ concentration and relative humidity conditions affect the calcium and carbonate ions concentration in the pore water. Scalenohedral calcite precipitates under non-

stoichiometric conditions with $[\text{Ca}^{2+}] > [\text{CO}_3^{2-}]$ while stoichiometric conditions with $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}] \approx 1$ promotes the growth of the rhombohedral calcite (Figure 5). Most importantly, modification in the calcite crystal habit from scalenohedron to rhombohedron is established in a CO_2 -rich atmosphere due to the dissolution-reprecipitation of calcite under low pH, leading to the protonation of the negatively charged scalenohedral faces and formation of rhombohedral faces having equal amounts of calcium and carbonate ions.²⁰⁾

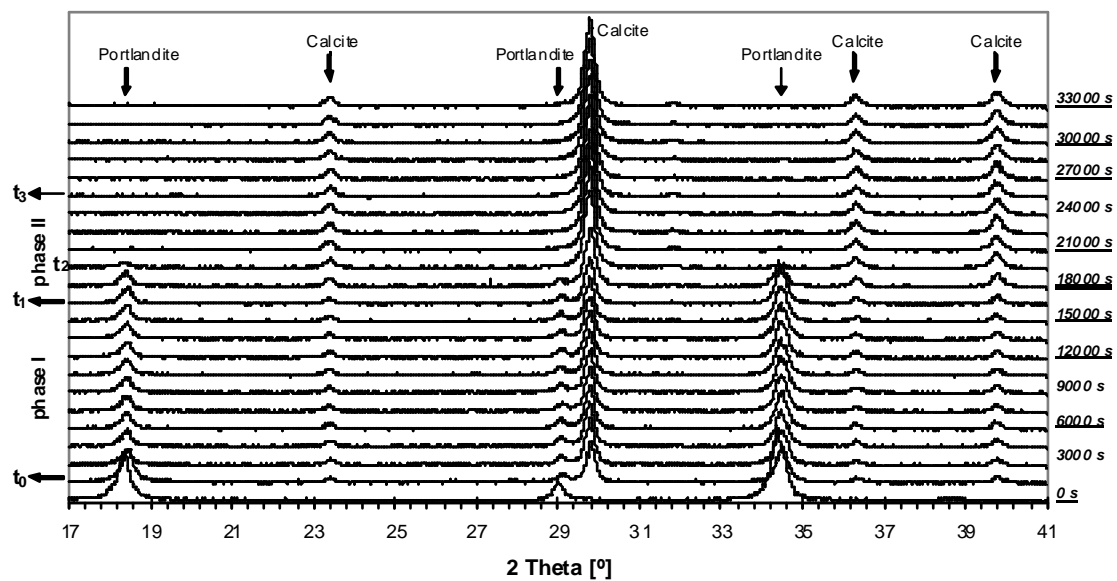


Figure 4: Sequential *in-situ* XRD patterns of lime paste during carbonation in a 100%- CO_2 atmosphere (t_0 : start of reaction; t_1 : start of increased CO_2 uptake; t_2 : time of maximum CO_2 uptake rate; t_3 : end of reaction).

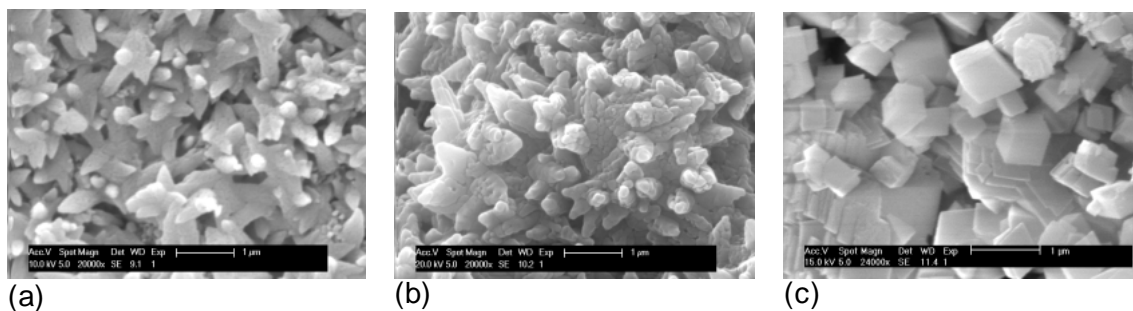


Figure 5: Calcite crystals precipitated on the exposed surface of a lime paste: scalenohedral calcite in air at 60% RH (a); scalenohedral calcite in air at ~93% RH (b); rhombohedral calcite in a 100%- CO_2 atmosphere at ~93% RH (c).

Besides the microstructural effects, carbonation also influences the chemical speciation and pore water chemistry of alkaline materials by introducing the carbonate/bicarbonate

species in the liquid system and by lowering pH. This has been extensively researched at the department of Chemical Engineering, in view of mechanistic understanding of weathering processes and subsequent long-term waste treatment assessment on the one hand and as a treatment method (accelerated carbonation) itself on the other hand. Heavy metal leaching is mainly controlled by the chemistry of abundant ions such as calcium, iron, silicate and sulfate by (co-)precipitation and sorption. Antimony for example forms calciumantimonates (roméites) in an environment that is both alkaline and rich in soluble calcium.²³⁾ The solubility of roméite can therefore be reduced by increasing calcium availability and pH, for instance by adding lime to wastes. Carbonation, however, increases calcium availability by lowering of the pH and subsequent dissolution of calcium containing minerals such as ettringite and strätlingite (Figure 6). This increased calcium availability could in turn decrease antimony leaching, but this effect is retarded due to the lower pH. In addition, prolonged carbonation allows neoformed iron and aluminium (hydr)oxides to precipitate, which, combined with the lower pH, induces significant adsorption. Figure 7 shows that, depending on the carbonation conditions, it is possible to limit the increase of antimony leaching. Other metals such as copper exhibit a significant decrease in leaching due to carbonation (Figure 7).^{8,13)} This is related with the effect of carbonation on the organic compounds that are still present in incinerator bottom ash, even after incineration.²¹⁾ In particular the hydrophilic and the fulvic acid fractions have been shown to control leaching of copper and are, at the same time, affected by an accelerated carbonation treatment. Carbonation decreases the solubility of these compounds by preferential biodegradation and adsorption to iron and aluminium (hydr)oxides, which in turn decreases copper leaching.

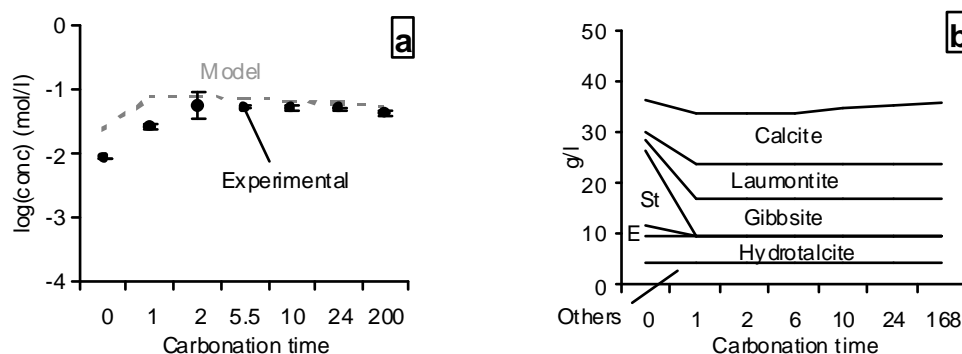


Figure 6: Experimental and modeled calcium leaching (a) and modeled mineral abundancy (b), as a function of carbonation time. “St” is Strätlingite, “E” is Ettringite.

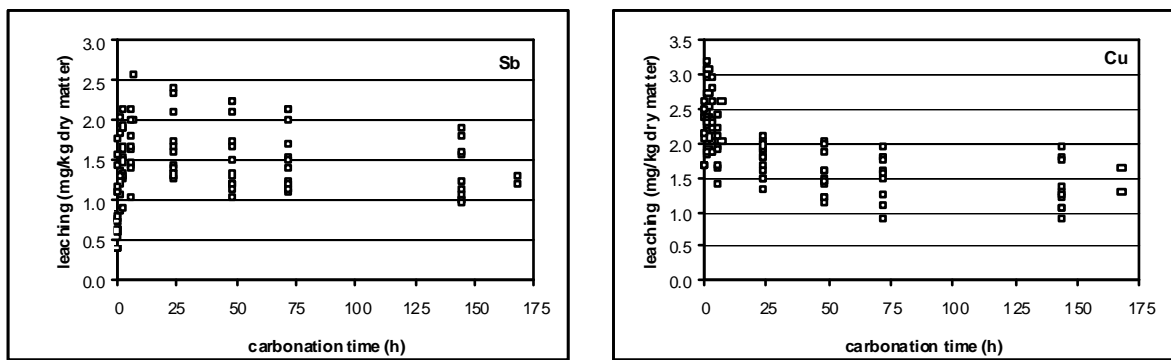


Figure 7: Leaching of antimony and copper as a function of carbonation time. The different data points at the same carbonation time indicate different processing conditions (temperature, CO₂ concentration, moisture content).

In blended waste-cement monoliths the carbonate introduction and pH decrease become decoupled.^{6,9)} Because of the presence of Calcium-Silicate-Hydrate, a key component in hydrated cement with a high pH buffering capacity, progressive carbonation first introduces carbonate in the pore water without decreasing pH. As a result, calcium leaching decreases. Only at a more advanced stage of carbonation does the pH decrease and carbonates are converted into bicarbonates, the salts of which are highly soluble. Therefore, calcium leaching from almost completely carbonated with mildly acidic leachant is higher than leaching from partially carbonated samples. Metals for which the carbonate salt is more soluble than the hydroxide go through a different scheme. Lead, for example, is soluble at high pH as a lead hydroxide complex. The very limited pH decrease in the first stage of carbonation shifts the equilibrium to the precipitated lead hydroxide, thus lowering lead leaching. With more advanced carbonation and significantly decreasing pH, lead hydroxide is converted into the soluble lead bicarbonate salt, thereby increasing lead leaching again.

Besides the effects on mineral speciation and pH, carbonation also affects porosity. Carbonation leads to an average decrease of porosity and a modified particle size distribution.¹⁰⁾ In blended waste-cement mortars it was found that the relative importance of small capillary pores (<0.1 µm) diminishes, whereas the proportion of larger capillary pores (> 0.1 µm) increases. The effect of carbonation-induced porosity decrease on leaching was shown to be significant for pH independent components such as sodium and, to a lesser extent, potassium. However, for heavy metals the pH effect of carbonation will be much more important.

With these studies, significant insights have been gained on the carbonation reaction mechanism in different materials such as lime mortars, lime-based hydraulic mortars, alkaline wastes and waste-cement blends. It has been confirmed that the role of water is one of the key parameters in the carbonation process in a porous system, which requires

a combined diffusion-dissolution process of CO₂. Complete carbonation cannot be achieved at high CO₂ concentrations if water is not present in sufficient amounts to allow the dissolution of CO₂. In addition, the use of industrial stack gas as a carbonating agent yields comparable results with the synthetic 10% CO₂ gas streams used in the laboratory. The pore structure built-up by the precipitated calcite also plays a critical role in the carbonation process as it should allow a continuous pore network for the diffusion process. Carbonation affects pollutant leaching significantly, and with correct understanding and improved control of process conditions, accelerated treatment may offer potential solutions for particular waste streams. To obtain a better understanding of the carbonation mechanism, the *in-situ* follow-up of the reaction progress is an essential tool.

Future research

In situ X-ray powder diffraction (XRPD) experiments allow to identify and quantify the crystalline phases in complex reacting systems such as carbonation reactions, pozzolanic-lime reactions or the hydration reactions of blended cements. In addition, an assessment of the total amount of amorphous phases can be made. The recent advent of synchrotron X-ray sources and efficient X-ray detector systems renders time-resolved diffraction studies possible and enables to study the details of the kinetics and mechanism of the reaction at early ages. An example of the results obtained by an *in situ* synchrotron X-ray powder diffraction (XRPD) experiment is given in Figure 8, where the pozzolanic reaction of lime with the natural zeolite (K-exchanged) clinoptilolite is investigated.²⁶⁾ XRPD measurements for quantitative analysis were recorded at the BM01b beam line for high resolution powder diffraction at the European Synchrotron Radiation Facility. This technique will be introduced in the carbonation research as well.

Research on carbonation will also continue with an in-depth research on the reaction term and on the diffusion term. The former will investigate mastering lime mortar and hydraulic mortar carbonation under atmospheric conditions using chemical admixtures for the purpose of enhancing the reaction for on-site applications. The latter will focus on modelling the diffusion process in relation to different water contents and pore structures in order to have a better understanding of the carbonation reaction mechanism in mortars.

Work on processing conditions will focus on the area of mineral carbon sequestration in alkaline waste materials (metallurgical slags and incinerators ash) as well as reference materials such as olivine and serpentine. Besides the more conventional process parameters (temperature, pH, moisture content, particle size and specific surface area), attention will be given to the application of local energy sources to remove carbonated

shells from uncarbonated cores and to improve reactant diffusion in the reaction zone of the liquid layer.

Collaborative research in the future is thus planned along the established focus lines of *in-situ* analysis, processing conditions and product properties. The range of materials investigated will be extended to take into account all alkaline materials (not only hydrated mortars and ash, but also metallurgical slag and primary raw materials). Also the link between microstructure and the upstream high-temperature processes will be explored in collaboration with the department of Metallurgy and Materials Engineering.

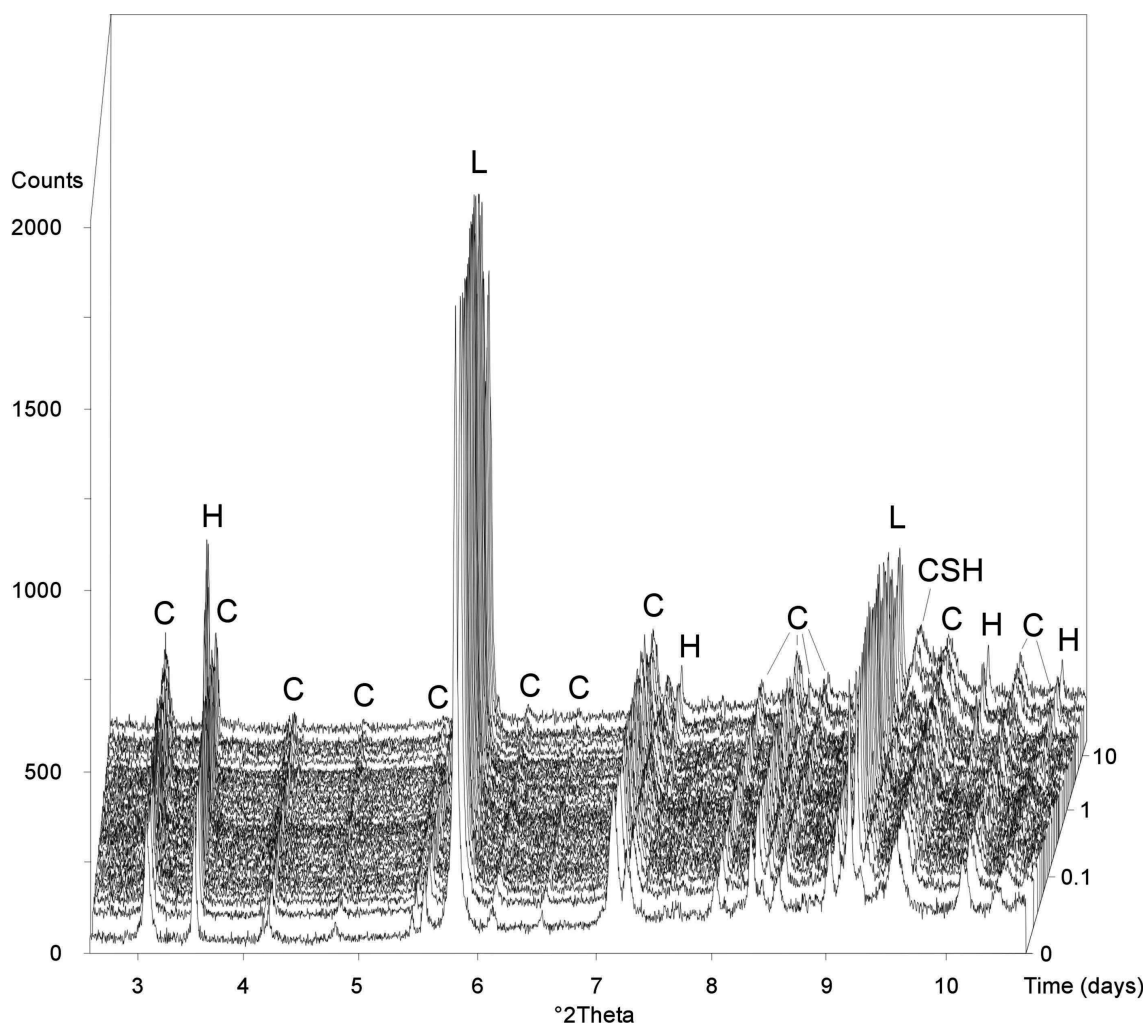


Figure 8: Time-resolved in situ synchrotron XRPD patterns of the pozzolanic reaction between K-exchanged clinoptilolite (C) and lime (L), with the formation of the semi-amorphous Calcium-Silicate-Hydrate phase (CSH) and hydrocalumite (H).

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Aqueous Mineral Carbonation and its Effect on Speciation and Leaching Properties of Major and Minor Elements in Steel Slag

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Abstract

This paper reviews a number of recent studies in which the authors have focused on the mineral carbonation mechanisms and potential of steel slag, as well as on the leaching properties of freshly produced steel slag and steel slag at various degrees of carbonation. By combining controlled carbonation and leaching experiments, geochemical modelling and mineralogical analyses, these studies are designed to contribute to the development of a treatment process that can facilitate the beneficial utilisation of steel slag. The treatment is focused on capturing some of the atmospheric CO₂ emissions of the steel-making process and, simultaneously, on reducing emissions of leached contaminants to soil and groundwater during the utilisation of steel slag in construction applications.

Introduction

Converter steel slag is the predominant solid-residue formed during the production of steel. It is typically formed at rates of 90-100 kg of steel slag per tonne of steel in the LD/converter process during the refining of hot metal from the blast furnace. The slag is frequently used as a secondary aggregate in construction applications, but imposes a high pH (12.5) and low Eh, which may exert adverse effects in aqueous environments with limited water flow. These properties are related to the slag mineralogy: hydration of the highly alkaline C₂S and lime (CaO) phases buffers the pH of interstitial water at a value of approximately 12.5, while the presence of divalent iron in Wuestite gives rise to reducing Eh values.¹⁾

The substantial content of highly alkaline mineral phases, as well as the large production of CO₂ in the steelmaking process, has caused steel slag to be considered as feedstock for aqueous mineral carbonation, as a possible technology to reduce atmospheric CO₂ emissions.²⁾ The use of alkaline industrial residues, such as steel slag, is potentially attractive for this purpose because of their availability in industrial areas,

low costs and possibly higher reactivity, relative to mineral ores. Although their total CO₂ sequestration capacity is limited relative to total anthropogenic CO₂ emissions, the use of residues as feedstock can contribute to make the first mineral CO₂ sequestration (demonstration) plants economically feasible.²⁾

In addition to its possible contribution to the reduction of CO₂ emissions, carbonation of alkaline solid residues has been demonstrated to have potentially beneficial effects on the leaching of constituents from these materials to the environment. For example, reduced leaching of potentially harmful constituents has been reported for residues such as municipal solid waste incineration (MSWI) bottom ash, fly ash from coal fired power plants, air pollution control residues, and steel slag (see Huijgen & Comans³⁾, and references therein). In such studies, a number of possible carbonation mechanisms has been distinguished that affect leaching, such as (1) precipitation of carbonates, (2) pH-neutralisation, (3) formation of minerals other than carbonates, (4) co-precipitation and (5) sorption on freshly precipitated surfaces. Leaching experiments combined with geochemical modelling, and mineralogical characterisation (*e.g.* by X-ray diffraction and electron microscopic analyses) have been shown to be valuable tools to study the leaching properties and underlying mechanisms of these residues.

This paper reviews a number of recent studies in which the authors have focused on the mineral carbonation mechanisms and potential of steel slag, as well as on the leaching properties of freshly produced steel slag and steel slag at various degrees of carbonation. By combining controlled carbonation and leaching experiments, geochemical modelling and mineralogical analyses, these studies are aimed to provide a mechanistic insight into (1) the mineral CO₂ sequestration potential of steel slag and (2) the effects of the carbonation processes on the leaching properties of steel slag, including pH, redox potential (Eh), major and trace elements. As such, these studies are intended to contribute to the development of a treatment process that can facilitate the beneficial utilisation of steel slag.

Materials and Methods

Steel slag samples

Two types of converter slags have been selected for carbonation experiments at atmospheric pressure (see below), each derived from a single heat, representing the maximum difference in primary mineralogy: K1 slag, which consists mainly of C₂S (2CaO.(Si,P,V)O₄), C₂F (2CaO.(Fe,Ti,Al,V)₂O₃) and magnesio-wuestite (MW; (Fe,Mg,Mn)O), and K3 slag, which contains C₃S (Ca₃SiO₅), C₂S, C₂F, MW and free-lime (CaO).¹⁾ The C₃S is a high-temperature phase which decomposes to C₂S + lime during cooling, but leaves a characteristic intergrowth texture, possibly with a different

reactivity for CO₂. Both slags were air-cooled and subsequently broken and sieved to obtain a representative 2-3.3 mm fraction of 25 kg starting material for the experiments. A third batch of steel slag, very similar to the K3 slag, was used for the carbonation experiments at elevated pressure (see below).⁴⁾

Carbonation experiments

Carbonation experiments at elevated pressure and temperature have been performed in a 450 ml autoclave reactor. For specific experimental details the reader is referred to Huijgen *et al.*⁴⁾ A suspension of steel slag and nanopure-demineralised water was stirred at a specific liquid to solid (L/S) ratio and stirring rate. The reactor was closed and heated to the reaction temperature ($T = 25-225^{\circ}\text{C}$) and maintained at that temperature during the reaction time ($t = 2-30$ min). When the temperature had reached the set point, CO₂ was added directly into the solution using a gas booster until a specific CO₂ pressure was established ($p_{\text{CO}_2} = 1-30$ bar). During the reaction time, the CO₂ pressure was kept constant within ± 0.2 bar of the set point by replenishment of the consumed CO₂. When the reaction time had elapsed, the addition of CO₂ was stopped and the autoclave was cooled down to 40°C, depressurised and opened. The suspension was immediately filtered quantitatively over a 0.2 µm membrane filter and the solid was dried overnight at 50°C in an oven. Finally, the product was analysed to determine the conversion of the reaction. During the experiment, the temperature of the reactor and the heating jacket and the total pressure inside the reactor were recorded with a data acquisition unit. The partial CO₂ pressure was calculated from the total pressure and the water vapour and air pressure corresponding with the temperature inside the reactor.

Carbonation experiments at atmospheric pressure were performed in a glass column (inner diameter 5 cm, 20 cm length) with a thermostatic jacket. About 900 g steel slag was wetted and placed in the column. A CO₂/Ar gas mixture was water-saturated at elevated temperature, to ensure the presence of water in the experiments, and was introduced in an up-flow direction at a flow rate of about 400 ml/min. Experiments were performed at temperatures between 5 and 90°C under water-saturated and under-saturated exposure and reaction times of 8-200 h (van der Laan *et al.*¹⁾).

Determination of carbonate content in steel slag

The carbonation efficiency was quantified by thermogravimetric analysis (Mettler-Toledo TGA/SDTA 851e) coupled to a Pfeiffer (thermostar) Quadrupole mass spectrometer (TGA-MS). 20-50 mg steel slag (<106 µm) was weighed in a ceramic cup and heated from 25-1100 °C under a nitrogen atmosphere at a heating rate of 40 °C/min. The weight loss was recorded by the TGA microbalance. The MS simultaneously monitored the evolved gases for CO₂. The CO₂ peak area was determined by integration and the amount of evolved CO₂ was calculated from a calibration line based on the decomposition of CaCO₃ standards. Further details are provided in Huijgen *et al.*⁴⁾

Characterisation of leaching processes

The pH-dependent leaching characteristics of both the fresh and carbonated steel slag samples were determined in a pH-stat system. Eight suspensions of a slag sample and Nanopure-demineralised water, at an initial liquid to solid (L/S) ratio of 10 L/kg, were stirred for 48 h in closed Teflon reaction vessels at room temperature. For seven vessels, the pH was controlled automatically ± 0.2 pH units around a pre-set pH-value (pH = 2–12.5) by the addition of 1 or 5 M HNO₃ and 1 M NaOH. For one vessel, the pH was not adjusted and leaching was performed at the native pH of the sample. After 48 h, the pH and redox potential of the suspensions were determined and the suspensions were filtered through 0.2 μ m filters.

Column leaching (percolation) tests were performed according to CEN/TS 14405. The steel slag was added to a borosilicate glass column (inner diameter 5 cm) in layers of a few cm and packed by shaking and pushing gently with a rod to a filling height of ± 20 cm. Nanopure demineralised water was used as the leachant. The packed columns were water-saturated and pre-equilibrated for 72 hours, as prescribed by CEN/TS 14405, after which the influent was pumped in up-flow direction. Computer-controlled flow controllers assured a constant flow velocity during the experiments. Fractions were collected automatically at cumulative L/S values of 0.1, 0.2, 0.5, 1, 2, 5 and 10 (l/kg). Effluent fractions were collected in acid-cleaned PE bottles. Shortly after collection of each effluent fraction, pH, redox potential (Eh) and conductivity were determined, and sub-samples for chemical analysis were taken and filtered through 0.45 μ m membrane filters.

The filtered leachates from the pH-stat and column experiments were analysed for a large number of major and trace elements.^{1,3)}

Geochemical Modelling

Geochemical modelling was performed on pH-stat leachates and process water samples from the carbonation experiments to identify the leaching processes. Details of the model set up in the geochemical modelling framework ORCHESTRA, considering aqueous speciation, mineral dissolution/precipitation and sorption processes, are provided by Huijgen & Comans.³⁾ Selective chemical extractions were performed on the fresh and carbonated pH-stat samples to obtain model input parameters for the amounts of reactive amorphous and crystalline Al-, Fe- and Mn-(hydr)oxide minerals in the steel slag matrix, which were considered to potentially control sorption processes.³⁾ The element concentrations in the leachates were modelled over the entire pH range. For all sorbates except Mo, the measured concentration at pH = 2 was taken as an estimate of their availability (*i.e.*, the maximum fraction of an element that can be leached), since it was assumed that the available element fraction is completely leached at this pH. For (anionic) Mo, the highest concentration was measured at alkaline pH-range and taken as

the availability (e.g., at pH = 8). Verification of these assumptions by modelling for each individual sorbate showed that at most 8% remained sorbed at these pH values.

Mineralogical characterisation

The mineralogical composition of fresh and carbonated steel slag samples was determined using powder X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) with energy-dispersive X-ray (EDX)-spot analysis, according to van der Laan *et al.*¹⁾ (K1 and K3 samples used for carbonation at atmospheric pressure) and Huijgen *et al.*⁴⁾ (slag samples used for high-pressure carbonation).

Results and Discussion

Figure 1 shows a typical SEM-micrograph of a (polished) steel slag sample that was carbonated in the autoclave at (near optimal) conditions of $T = 150^{\circ}\text{C}$ and $p_{\text{CO}_2} = 20$ bar. As a result of the carbonation process, a coating was observed to develop at the steel slag surface, with a composition that was identified as CaCO_3 by SEM/EDX-analysis. No separate calcium carbonate particles were identified in the carbonated sample. Further examination of the polished samples has revealed three other phases: (1) an iron rich phase (C_2F , indicated in Fig.1 as Ca-Fe-O), (2) a calcium silicate phase (C_2S) and (3) a SiO_2 phase with only traces of Ca. The first two phases are present in both the non-carbonated and the carbonated slag, while the SiO_2 and CaCO_3 were only identified in the carbonated material.

Three major phases of calcium have been identified in the fresh steel slag, on the basis of XRD and SEM analyses:⁴⁾ $\text{Ca}(\text{OH})_2$, Ca-(Fe)-silicates and C_2F . Based on their solubility and previous carbonation experiments, a lower carbonation rate is expected for Ca-silicates relative to Ca-(hydr)oxides. Portlandite was completely converted to calcite at the applied carbonation conditions. These differences in solubility and, hence, the availability of Ca for carbonation, are also reflected in the pH-dependent leaching of Ca in Figure 1. Two steps can be distinguished at which the Ca leaching increases strongly. The first step occurs between pH 11.1 and 9.6, at which 29.6% of the total Ca content is leached. This fraction is defined as fraction I and probably consists mainly of portlandite and Ca-silicates (similar to CSH) that are relatively easily leachable. The second step occurs between pH 5.1 and 3.5, at which in total 61.6% of the Ca is dissolved. This fraction (II) represents an additional Ca release of 32.0% and is assumed to consist of Ca-silicates (such as C_2S) that are more difficult to dissolve. The rest (Ca-fraction III, 38.4% of the total Ca) represents virtually non-available Ca, at this particular particle size and leaching time, and possibly corresponds with the C_2F phase.

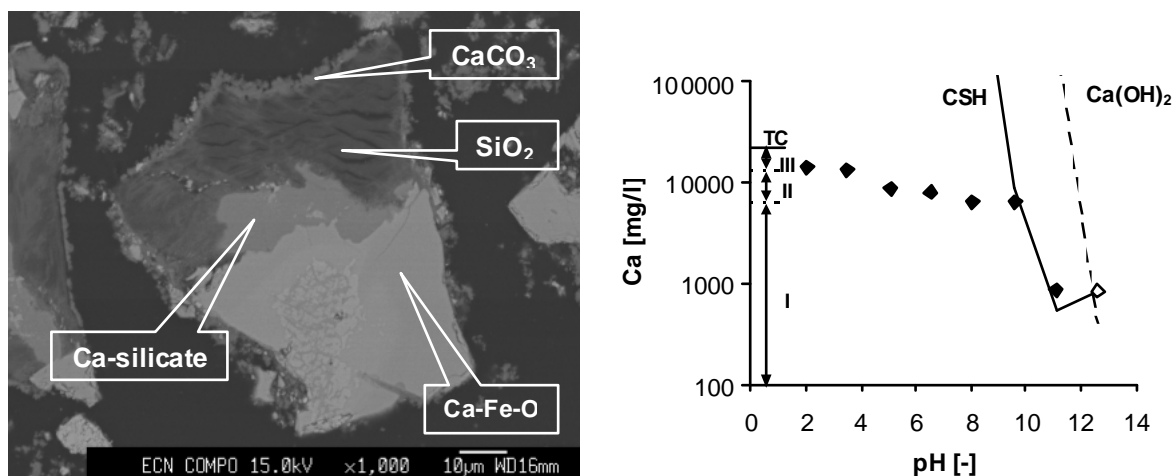


Figure 1: SEM backscattered electron micrograph of a polished carbonated steel slag particle ($p_{\text{CO}_2} = 20$ bar, $T = 150$ °C, $t = 30$ min, $d < 106$ μm) embedded in resin, with SEM-EDX analysis (left, Huijgen *et al.*⁴⁾). Ca- and Si-leaching characteristics of fresh steel slag (< 106 μm) and geochemical modelling of solubility control by specific minerals. Total Ca content (TC) and Ca-fractions I, II and III are indicated. Open symbols indicate the native pH of the sample. Solubility products of Ca(OH)_2 (portlandite), amorphous SiO_2 and CSH ($\text{Ca}_{0.8}\text{SiO}_5\text{H}_{4.4}$) were used to calculate the solubility curves (right, Huijgen *et al.*⁴⁾)

Figure 2 compares the carbonation of steel slag in the autoclave at $P = 20$ bar with that of the Ca-silicate mineral wollastonite, as a function of the reaction temperature. The shape of the curve and the optimum temperature are similar for both materials. However, steel slag shows a higher conversion, especially at low temperatures, which confirms its lower (geo)chemical stability and greater susceptibility to carbonation.⁴⁾ It is interesting to note that during the carbonation of both steel slag and wollastonite, the formation of a SiO_2 -rim was observed (as shown in Fig. 1 for steel slag). Calcite was found to precipitate only at the surface of the steel slag particles while it was formed both as separate mineral particles and at the particle surfaces during the carbonation of wollastonite. Below the optimum temperature, the carbonation rate was found to be controlled by the leaching of Ca, particularly given observations that the mean particle size was the key process variable via the specific surface area,^{4,5)} which is likely determined by the Ca-diffusion rate through the silicate rim. At the higher reaction temperatures the nucleation and growth of calcite is the probable controlling process.⁵⁾

The right-hand panel in Figure 2 shows the amount of CO_2 sequestered during the carbonation of K1 and K3 steel slag at atmospheric pressure, as a function of time (at 90°C) and under both water-saturated and unsaturated conditions.¹⁾ Given the particular aim of these experiments to identify the effect of carbonation on the leaching properties of steel slag, relatively large (2-3.3 mm) steel slag grains were used, with a limited

surface area. As a result, only low degrees of carbonation are reached. Also in these experiments, the reaction was generally found to proceed fastest at higher temperature (50-90°C) and at water-saturated conditions. Consistent with its content of free lime, the K3-slag is more prone to carbonation (about 15 g CO₂/kg) than K1-slag (about 6 g CO₂/kg). Figure 2 shows that the carbonation rate at water-saturated conditions declines strongly after about 24 h.

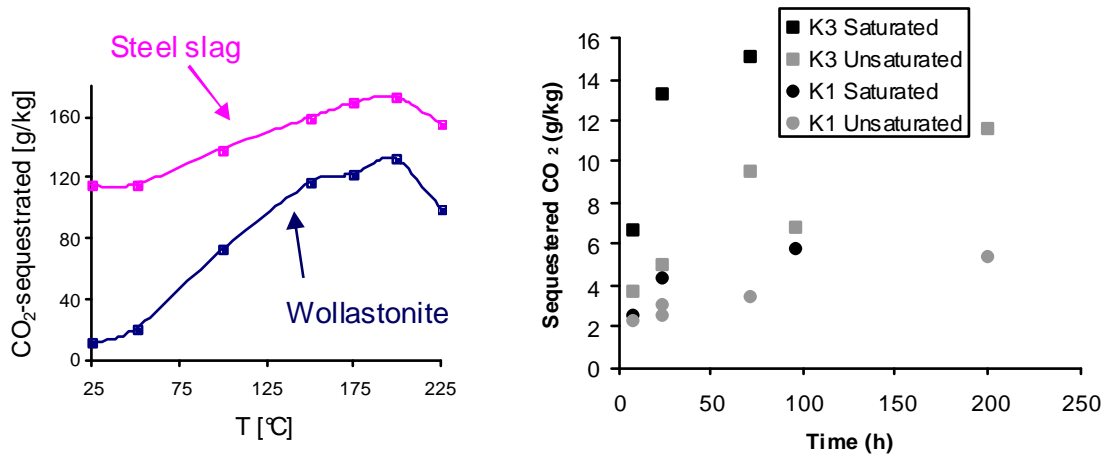


Figure 2: Captured CO₂ as a function of temperature under water-saturated conditions at $P = 20$ bar and $t = 30$ min for fine grained ($< 106 \mu\text{m}$) steel slag and wollastonite (left; Huijgen *et al.*⁵⁾) and as a function of reaction time under water-saturated and unsaturated conditions for larger (2-3.3 mm) K1 and K3 steel slag particles at atmospheric pressure and $T = 90^\circ\text{C}$ (right; van der Laan *et al.*¹⁾)

Figure 3 shows the pH-dependent leaching properties of a number of major and minor elements for finely ground steel slag before carbonation and at two different levels of carbonation. The behaviour of the following three categories of elements is distinguished and briefly discussed below: (1) Ca and Si, which play a major role in the carbonation reactions, (2) Al, Fe and Mn, which form reactive (hydr)oxide surfaces that may contribute to limiting the leaching of contaminants; and (3) Oxyanionic and metal contaminants that are potentially harmful to the environment.

Calcium and Silicon

Calcium leaching is initially (at pH ~ 12.5) controlled by the solubility of portlandite and dissolves rapidly as the pH is lowered. Given the corresponding leaching of Si, this behaviour is most adequately modelled on the basis of the solubility of CSH. However, ettringite is also calculated to be close to saturation in the fresh slag and may contribute to the rapid initial Ca release and carbonation.³⁾ During carbonation, the initial Ca-minerals are (partly) converted to less-soluble calcite and the leaching curves for 30 and 60% carbonated slag tend towards the calcite solubility curve. However, as frequently

observed for carbonated secondary materials, the leachates remain oversaturated with respect to calcite (Meima & Comans⁶⁾ and references therein).

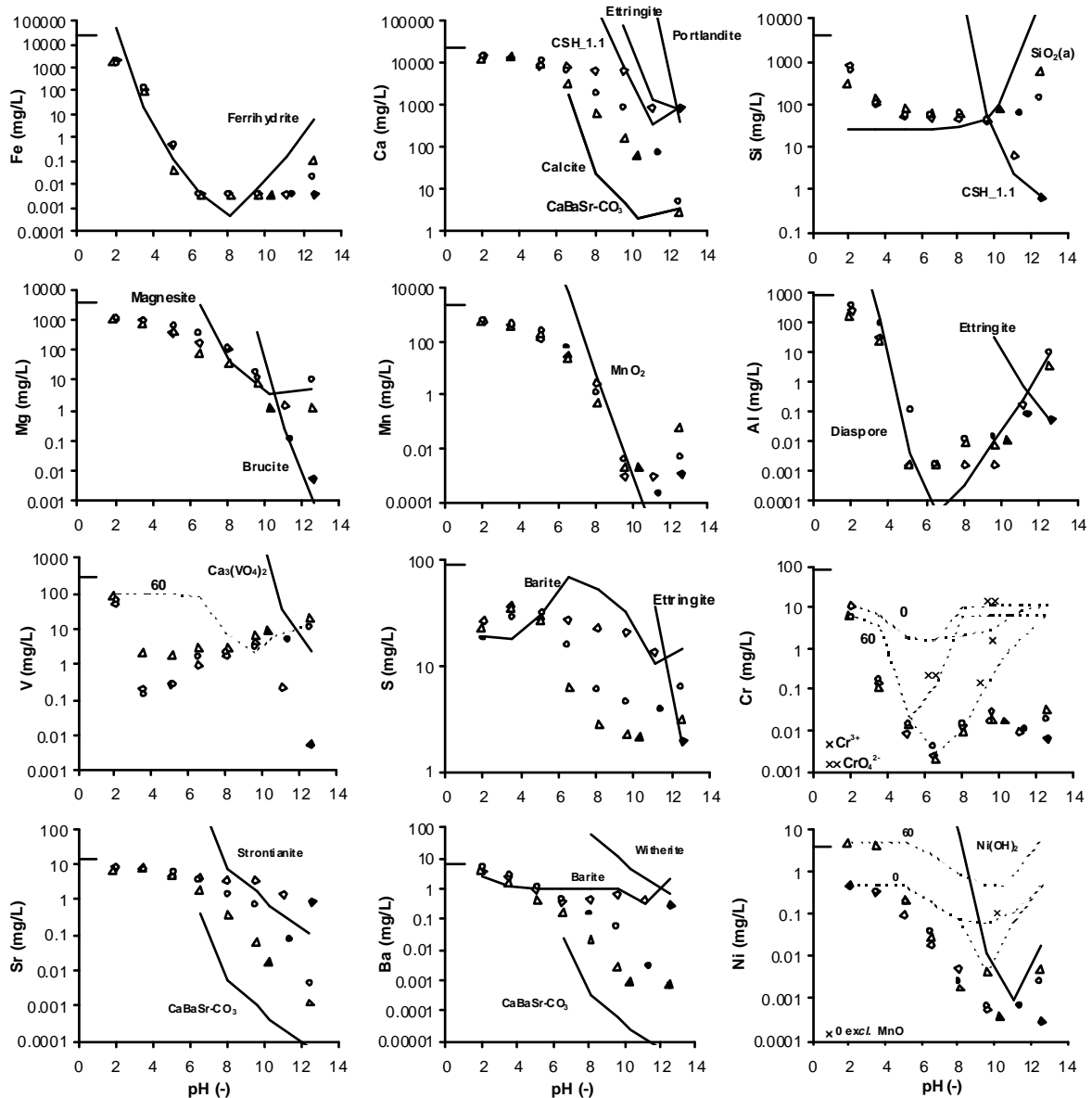


Figure 3: pH-dependent leaching curves of major and selected trace elements for finely ground (30-40 μm) fresh steel slag (\diamond) and carbonated samples with 30% (\circ) and 60% (Δ) Ca-conversion (carbonated at $T = 30^\circ\text{C}/p_{\text{CO}_2} = 2$ bar and $T = 150^\circ\text{C}/p_{\text{CO}_2} = 20$ bar, resp.). Solid symbols indicate the native pH of the samples. Selected modelling results are shown for the leachates of the fresh and 60% carbonated sample, either on the basis of solubility control by a specific mineral or solid solution (full line) or on sorption processes (dashed line). Short horizontal lines represent the total amount present in the fresh steel slag.³⁾

The carbonated samples are strongly undersaturated with respect to portlandite and ettringite, while the leachates remain close to equilibrium with CSH. The increasing Si concentrations in these leachates towards high pH are consistent with the solubility pattern for amorphous SiO_2 , suggesting that CSH is at least partially carbonated. These observations suggest that Ca-fractions I and II (see above) are largely converted.

Reactive Al-, Fe-, and Mn-(hydr)oxides

For all samples, the leaching of Al is adequately described by the solubility of diaspore (AlOOH), except at the native pH for the non-carbonated sample, where ettringite is probably present. Similarly, the leaching of Fe can be described by ferrihydrite (amorphous $\text{Fe}(\text{OH})_3$), except at high pH. The strongly increasing Mn concentrations in the leachates below pH 11 is adequately described by MnO_2 . The selective extractions have shown that the amount of Al- and Fe-(hydr)oxides increases with the carbonation degree, but not that of Mn-(hydr)oxides. The Fe-(hydr)oxides formed at the lower reaction temperature (30°C; 30% carbonated sample) are mainly amorphous (with higher surface area and, hence, reactivity), while at the higher temperatures (150-200°C; 60% carbonated sample) mainly crystalline Fe-(hydr)oxides are formed. This observation suggests that carbonation at lower temperature results in a higher reactive surface that contributes to the retention (and thus lower leaching) of metallic and oxyanionic contaminants.

Heavy metals and oxyanions

The leaching of the cationic metals Cr(III), Ni, Co and Zn is best described on the basis of their adsorption to the reactive Al-, Fe-, and Mn-(hydr)oxide surfaces, except at pH > 9.5 at which the solubility of the metal(hydr)oxides is likely to control leaching.³⁾ These adsorption processes are believed to play an important role in controlling the environmental quality of steel slag. Research focusing on the contribution of individual reactive mineral surfaces, the quantification of their reactive surface area, and the development of more accurate sorption parameters, is important to facilitate the development of methods to further improve the environmental quality of bottom ash.

The leaching of V is of particular concern, given its substantial concentration in steel slag. As Figure 3 shows, V leaching at the native pH (~ 12.5) of fresh steel slag is low, but increases by 2-3 orders of magnitude after carbonation at the levels obtained for this finely ground sample in the autoclave. The initial leaching is probably controlled by alkaline Ca-phases (particularly C_2S) in which V is incorporated, while after carbonation it is likely controlled by sorption to reactive mineral surfaces.

Figure 4 shows the cumulative release of V and the leachate pH in the percolation tests with the coarser K1 and K3 slag particles, before and after carbonation at atmospheric

pressure at water-saturated and -unsaturated conditions. The pH of the treated slag showed a short-lived improvement, starting at 9.5 but with a rebound to 10.5-11 for K1 and back to the original pH of 12.5 for K3 slag after 48 hrs of water contact.¹⁾ Initially, the surface carbonation was effective in neutralising the pH, as observed for the more finely ground (K3-type) particles carbonated in the autoclave (Figure 3).

Improved pH goes along with higher V-leaching, also similar to the results shown in Fig. 3. The K1 slag shows a particularly enhanced V-leaching up to 10-100 mg/kg, while the K3 slag remains within acceptable limits (< 1 mg/kg). A clear distinction is visible between the pH and vanadium leaching of the K1 and K3 slag. The K1 slag does not comply with the limit values for a category 1 application in the Dutch Building Materials Decree (open application without isolation measures), while the K3 slag does comply with these criteria. However, vanadium leaching does also increase substantially after carbonation of K3 slag. Comparing the samples carbonated under unsaturated (lower degree of carbonation; see Fig. 2) with those carbonated under water-saturated conditions (higher degree of carbonation) shows that increasing the degree of carbonation is paralleled with further increasing vanadium leaching.

The pH of the untreated K1 slag, at each L/S ratio, is substantially lower than the pH of the K3 slag, which is caused by the absence of CaO in the K1 slag, while free lime is present in the K3 slag. As Figure 4 shows, carbonation of the K1 slag reduces the pH of the material, while the pH of the K3 slag is not significantly influenced. Carbonation was found to occur only at the surface of the grains in both the K1 and K3 slag. During the carbonation treatment, portlandite is also partly formed from CaO inside the grains of K3 slag. This process results in the formation of cracks due to volume expansion, resulting in a slow (diffusive) release of alkalinity from unreacted portlandite in the inner grains. Since the K1 slag does not contain CaO, this material does not crack and largely maintains its reduced pH after carbonation.

Microscopic characterisation of the spatial mineral patterns in carbonated K1 and K3 slag have shown that the calcite and amorphous silicate reaction products of the CaO (K3) and C2S (K1 and K3) conversion do not sufficiently envelope the slag grains to improve the environmental properties with respect to pH and V-leaching in a sustainable manner.¹⁾ The carbonation treatment of particularly the K1 slag (without CaO) is still insufficient to comply with the criteria of the Dutch Building Materials Decree. Further research is currently focusing on options to optimise the carbonation treatment of steel slag and to evaluate the development of the pH and leaching properties of steel slag in specific environmental utilisation scenarios. The geochemical modelling approach described above forms an important tool for both of these objectives. We are further developing this approach on the basis of microscopic characterisation of steel slag mineral phases and the implementation of thermodynamic

solubility data for cement minerals that are currently lacking in generic thermodynamic databases of most geochemical modelling platforms.

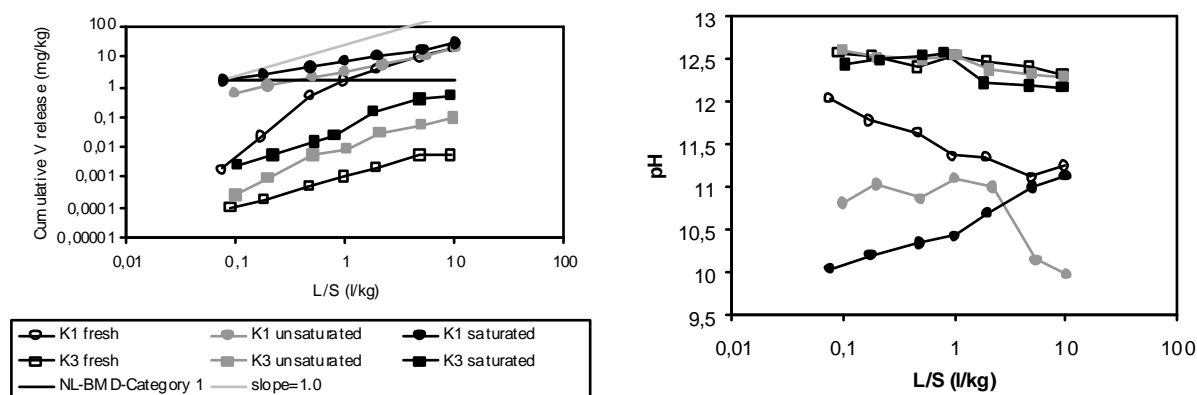


Figure 4: Cumulative release of V (left) and leachate pH (right) as a function of liquid/solid (L/S) ratio for fresh and carbonated K1 and K3 slag, under both water-saturated and unsaturated conditions (van der Laan *et al.*¹⁾)

Conclusions

Carbonation experiments with finely ground steel slag at elevated temperature and CO₂-pressure in an autoclave have shown that this material provides a very reactive feedstock for the purposes of mineral CO₂ sequestration. The carbonation reaction is observed to occur in two steps: (1) leaching of calcium from alkaline steel slag minerals into the solution and (2) precipitation of calcite on the surface of these particles. The first step and, more in particular, the diffusion of calcium through the solid matrix towards the surface, appears to be the rate determining reaction step. This step is found to be hindered by the formation of a CaCO₃-coating and a Ca-depleted (amorphous) silicate zone during the carbonation process. Very similar features have been observed for larger steel slag particles that have been carbonated at atmospheric pressure, for the purpose of improvement of their environmental leaching properties.

Leaching experiments, geochemical modelling and microscopic characterisation of spatial mineral patterns in steel slag with (K3) and without (K1) free CaO have shown that the calcite and amorphous silicate reaction products of the CaO (K3) and C₂S (K1 and K3) conversion do not sufficiently envelope the slag grains to improve the environmental properties with respect to pH in a sustainable manner. Moreover, the carbonation treatment is observed to enhance the leaching of V substantially, particularly from the K1 slag, which would cause non-compliance with the criteria of the Dutch Building Materials Decree.

Further research is currently focusing on options to optimise the carbonation treatment of steel slag and to evaluate the development of the pH and leaching properties of steel slag in specific environmental utilisation scenarios. The geochemical modelling approach described above forms an important tool for these objectives. We are further developing this approach on the basis of microscopic characterisation of steel slag mineral phases and the implementation of thermodynamic solubility data for cement minerals that are currently lacking in generic thermodynamic databases of geochemical modelling platforms.

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Accelerated Mineral Carbonation of Steel Slags

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Abstract

Accelerated carbonation of stainless steel slag is the focus of this paper. The work aimed at assessing the CO₂ storage capacity of various size fractions of stainless steel slag under mild operating conditions, studying the influence on kinetics of some operational parameters (temperature, pressure and liquid to solid ratio), and investigating the effects of carbonation on the mineralogy and leaching behaviour of the residues. Maximum CO₂ uptakes of 130 g CO₂/kg slag were achieved in the finest fraction. Carbonation kinetics were relatively fast, achieving completion in around 1 hour with a CO₂ pressure of 3 bar and an optimal liquid to solid ratio of 0.4 l/kg; temperature was the parameter that most influenced CO₂ uptake, due to enhancement of silicates dissolution. The mineralogy of the ash was affected by the treatment, showing a significant reduction of Ca and Mg oxides, a slight decrease of silicate phases (Ca₂SiO₄), and a significant increase of calcite, as well as the formation of dolomite. The leaching behaviour of the carbonated ash was also modified, exhibiting a pH reduction by 1-2 units depending on particle size, a decrease of Ca leaching and an increase of Si leaching. Cr, which was the only trace compound significantly leached, in particular from the finer grain size classes, was not appreciably affected by carbonation.

Introduction

In developed countries various industrial processes including fossil fuel combustion, cement production, iron and steel manufacturing and others are among the major point-source contributors to the input of anthropogenic CO₂ into the atmosphere. In particular, the steel industry is globally the largest energy consuming manufacturing sector, and accounts for 7–12% of anthropogenic greenhouse gas (GHG) emissions,¹⁾ several measures, such as scrap steel recycling, are hence being developed to improve energy efficiency and cut CO₂ emissions, but more drastic measures are needed if the reduction targets established by the Kyoto Protocol are to be achieved.

Along with the emissions of GHGs from the mentioned industrial processes, considerable amounts of solid residues are also generated, which are either variously reused in different applications or finally landfilled; in either case, the predominantly

inorganic constituents (heavy metals, metalloids and alkalies) associated to these residues may be released to the environment, with potential environmental impacts on terrestrial ecosystems and human health. For such reasons, careful control of atmospheric emissions and appropriate management of the solid residues generated are both claimed in view of attaining environmental sustainability. Within this framework, a combined approach aiming at reducing the CO₂ emissions, at the same time improving the environmental behaviour of the solid waste streams generated by a given industrial process, appears to be highly desirable.

Different strategies have been proposed to reduce CO₂ emissions from industrial activities, including decrease of energy consumption thanks to improved energy efficiency of the process, use of lower carbon content fuels, or downstream sequestration of the CO₂ produced. Carbon sequestration involves the capture and storage of CO₂ (CCS) in various sinks where carbon will be safely stored over geological timeframes. The potential CO₂ storage options include ocean disposal, injection into geological formations such as deep saline aquifers, oil reservoirs, mineral deposits and coal seams, as well as carbonation of alkaline industrial residues. Among these CO₂ disposal methods, mineral carbonation, as originally proposed by Seifritz²⁾, then first studied by Lackner *et al.*³⁻⁴⁾ and by numerous other investigators (see *e.g.* the literature review by Huijgen and Comans⁵⁾), is currently recognised as one of the most promising techniques.

Overview of the carbonation process

Mineral carbonation

The basic concept behind mineral carbonation is to mimic natural weathering of rocks. Mineral carbonation of alkaline minerals involves permanent storage of CO₂ under the thermodynamically stable forms of calcium or magnesium carbonates.⁶⁾ This process is based on acid-base reactions in which an acid (H₂CO_{3(aq)}) is neutralised by a solid base (alkaline mineral). Although several oxides or hydroxides of alkaline or alkaline earth metals can in principle be carbonated, Ca and Mg silicates are usually preferred, since they are available worldwide in large amounts. Mg-rich silicates such as olivine, serpentine and talc can be found in ultramafic rocks such as dunites, peridotites and serpentinites, whereas one of the preferred calcium containing silicate is wollastonite.⁵⁾ These minerals are available worldwide and have the potential of sequestering the total amount of CO₂ emitted from the combustion of all the available fossil fuel reservoirs.⁴⁾ Nevertheless, the CO₂ sequestration technology through mineral carbonation has not yet been developed at the full scale due to cost limitations.⁷⁾

An important aspect of mineral carbonation is the need to activate the surface of the

mineral to increase its effective carbonation yield. This can be done by a variety of physical or chemical pre-treatment methods, including size reduction, magnetic separation, thermal treatment, steam activation, acidic dissolution.^{7,8)} Upon activation, the mineral may be carbonated by two different routes;⁹⁾ the first one is an indirect route, by which the alkaline metal is first extracted from the silicate matrix and then precipitated as carbonate. Metal dissolution is the rate-controlling step of the whole process and may be enhanced either by adding a chemical agent^{10,11)} or by using elevated CO₂ pressure conditions.¹²⁾ To attain an effective carbonate precipitation, a two-stage silicate dissolution/carbonate precipitation process involving a pH shift from acidic to basic conditions has also been proposed.^{8,13)} The second route is a direct one, where the reactions occur either in the aqueous phase or at the gas-solid interface. In the aqueous process, carbonation occurs in a three-phase system (gas-water-solid medium), with considerably increased reaction rates if compared to the direct gas-solid process. Carbonation through the aqueous route occurs mainly in three steps, including Ca leaching from the solid matrix, contemporary CO₂ dissolution, and precipitation of calcium carbonate. The direct gas-solid carbonation process may present the most straightforward process route, as the carbonation reactions of Ca oxide and hydroxide are quite rapid. Conversely, although Mg(OH)₂ carbonation is fast enough for industrial use, under dry conditions the rate of MgO carbonation is too slow for significant amounts of CO₂ to be sequestered.¹⁴⁾

Carbonation of alkaline solid residues

Alkaline solid residues naturally mineralise upon contact with atmospheric CO₂ because they contain a variety of thermodynamically unstable minerals, including oxides, hydroxides and silicates, that can sorb CO₂ and convert it into the corresponding carbonate forms. Accelerated carbonation has been applied to many solid residue streams produced from coal fired power stations, including pulverized fly ash,^{15,16)} spent shale,¹⁵⁾ coal ash,¹⁷⁾ fluidised bed combustion ashes,¹⁸⁾ steel slag,^{16,19-25)} other types of combustion residues including de-inking ash,¹⁶⁾ paper mill ash¹⁶⁾ and ashes from municipal and special waste incineration,²⁶⁻²⁹⁾ cement-based materials.³⁰⁻³¹⁾ As all the above mentioned materials are often associated with CO₂ point-source emissions and tend to be chemically more unstable than geologically derived minerals, they require a lower degree of pre-treatment and less energy-intensive operating conditions to enhance carbonation yields.

Furthermore, after carbonation the leaching behaviour of alkaline waste materials such as coal ash,¹⁷⁾ oil shale ash,³²⁾ steel slag,³³⁾ incinerator bottom ash^{9,29,34)} and APC residues^{9,35,36)} is improved, allowing for use in civil engineering applications or for safer final disposal to landfills. In addition, carbonation has been shown to improve the mechanical properties of materials to be reused as aggregates, such as steel slag,^{16,37,38)} and enhance the sorption capacity of cement hydrates towards trace contaminants.³⁹⁾

With particular regard to iron and steelmaking slags, accelerated carbonation consists of two sequential processes: the dissolution of alkaline elements (Ca and Mg) from the silicate minerals and the precipitation of the corresponding carbonates. As outlined above, the two processes can be performed in single or double stage. In the latter case, dissolution and precipitation are optimised separately by selecting the proper pH with specific additives.²¹⁻²³⁾ The single-stage process has been carried out either in slurry phase, under high temperature (100–200°C) and moderate CO₂ pressures (10–30 bar),¹⁹⁾ or with partially humidified slag at lower temperatures and CO₂ pressures (30–50°C and 1–10 bar, respectively).^{16,38)} For slurry-phase carbonation, particle size was found to exert the most significant effects on the reaction; temperature was also shown to enhance silicates dissolution.¹⁹⁾

In this paper, the results from accelerated carbonation runs on four particle size fractions of stainless steel slag (SSS) are presented. The aims of the investigation were to assess the CO₂ uptake that can be achieved under mild operating conditions, identify the reacting species and the effects of operating variables on reaction kinetics, and analyse the effects of the treatment on the mineralogy and leaching behaviour of the slag.

Materials and methods

The SSS analysed in this study was a mixture of different residues produced at stainless steel manufacturing plant, *i.e.* the residues generated from the Electric Arc Furnace (EAF) and from the Argon Oxygen Decarburisation (AOD) converter units. A freshly produced 20 kg sample was collected at the plant, homogenised and dried at 50°C to constant weight. The slag was then divided by sieving into the following size fractions: 2–0.425 mm (class A); 0.425–0.177 mm (class B); 0.177–0.105 mm (class C); < 0.105 mm (class D). Class A was then milled to < 425 µm prior to chemical analysis and carbonation. Each fraction was thoroughly characterised in terms of physical properties, elemental composition, anion content, mineralogy and leaching behaviour.

Batch accelerated carbonation tests were performed in a pressurised stainless steel reactor equipped with a 150-ml internal Teflon vessel and placed in a thermostatic bath for temperature control. Gas humidity was maintained at 75% using a saturated NaCl solution in the reactor. In each run, three 1-g slag samples were mixed with deionised water at specific liquid to solid (L/S) ratios in the range 0–0.6 l/kg, placed in tin foil containers and exposed to a 100% CO₂ flow for preset times (0.5–24 h). Preliminary wet carbonation tests were run on class D slag to evaluate the influence of temperature (30–50°C), pressure (1–10 bar) and L/S ratio (0–0.6 l/kg) on the CO₂ uptake kinetics of the slag. Accelerated carbonation tests were then performed, under the optimal conditions determined for class D, on the other slag fractions and also on ungrinded class A to evaluate the influence of composition and specific surface area on the

carbonation yield. After treatment with CO₂, the samples were oven-dried at 50°C, and sample weight gain, which provides a first rough indication of carbonate formation, was recorded. The three samples treated in each run were grinded, since after treatment the slag exhibited a compact hardened structure, mixed together and analysed by calcimetry testing, to estimate the CO₂ uptake achieved by the treatment.

Results and discussion

The analysis of particle size distribution of the slag (see Figure 1) indicated that the residue could be classified as a sandy granular material with a significant (> 15 wt%) amount of fines (d < 100 µm). After discarding the 2-mm oversize fraction (< 10 wt%), the weight distribution of the slag into the 4 classes chosen for testing was: class A = 45.9 wt%, class B = 25.9 wt%, class C = 12.8 wt%, class D = 16.4 wt%

The elemental composition and anion content of the four size fractions investigated are reported in Table 1. The Ca content was very significant (40–50 wt%) and decreased with particle size. The same trend, although with considerably lower concentrations, was observed for Mg (2.2–4.5 wt%). Significant concentrations of Fe (4.3–6 wt%), Cr (3–4.2 wt%), Al (1.7–2.6 wt%), Mn (0.76–1 wt%) and V (0.09–0.15 wt%) were also measured and showed an increasing trend with particle size. Ni contents were quite lower than those found in other studies on stainless steel slag (0.04–0.075% as opposed to 0.2–0.45 wt%⁴⁰), probably due to differences in stainless steel manufacturing. As expected, the concentrations of other heavy metals and soluble salts were very low.

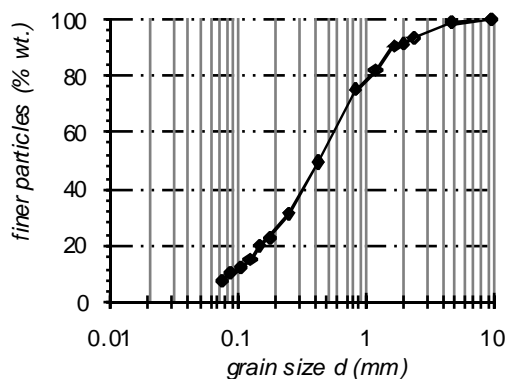


Figure 1: Particle size distribution of SSS

The results of the EN 12457-2 leaching test on untreated slag (Table 2) indicated that the pH of the eluates was high, above 12, and very similar for fractions B, C and D, decreasing slightly for class A. A declining trend with particle size was observed for Ca, Mg and Cr release. Cr, in particular, was the only trace compound that exhibited a higher leaching than prescribed for inert waste disposal (0.5 mg/l), which was nonetheless lower than values reported for AOD stainless steel slag.⁴⁰

Table 1: Elemental composition and anion content of the four size fractions of SSS

Element/anion	Class A	Class B	Class C	Class D
	(2-0.425 mm)	(0.425-0.177 mm)	(0.177-0.105 mm)	(< 0.105 mm)
Al (mg/kg)	26040	22080	17990	16840
As (mg/kg)	3.5	3.1	4.1	6.2
Ca (mg/kg)	432300	402000	445300	500300
Cd (mg/kg)	51.7	1.8	14.3	3.5
Cr (mg/kg)	42470	34070	29930	30470
Cu (mg/kg)	228	234.7	145.3	166.7
Fe (mg/kg)	59730	53000	43600	43270
K (mg/kg)	311	335	313	356
Mg (mg/kg)	22170	26470	29900	44600
Mn (mg/kg)	10450	8770	7870	7600
Mo (mg/kg)	231	187	168	225
Na (mg/kg)	1960	1890	1770	1540
Ni (mg/kg)	376	751	459	461
Pb (mg/kg)	76	77	58	120
Sb (mg/kg)	1.5	1.5	1.2	1.3
V (mg/kg)	1520	1130	813	920
Zn (mg/kg)	112	101	126	144
Cl ⁻ (%)	0.035	0.044	0.056	0.05
SO ₄ ²⁻ (%)	0.19	0.18	0.25	0.25
CO ₃ ²⁻ (%)	2.33	2.96	3.5	5.25

Table 2: Leaching test results before and after carbonation (2 h, 0.4 l/kg, 50 °C, 3 bar)

	Class A		Class B		Class C		Class D	
	untr.	carb.	untr.	carb.	untr.	carb.	untr.	carb.
pH	12.43	11.38	12.82	11.18	12.81	11.29	12.87	10.59
Ca (mg/l)	399	67	882.5	105	1025	84	1050	23.1
Cr (mg/l)	0.04	0.06	0.15	0.06	0.16	0.08	0.18	0.17
Fe (mg/l)	0.07	0.03	0.06	0.01	0.06	0.09	0.13	0.03
Mg (mg/l)	0.08	0.08	0.2	0.17	0.19	0.23	0.43	0.24
Si (mg/l)	1.6	67.5	0.9	63.8	1.2	51.3	1.6	7.3

XRD analyses allowed to identify several crystalline oxides and silicate phases in untreated SSS (Figure 2). Slag mineralogy did not appear to vary significantly with particle size: in all fractions a predominance of silicate phases including dicalciumsilicate, merwinite, akermanite, anorthite, gehlenite and forsterite were found. Cuspidine, a typical species formed during SSS hydration after addition of fluorine, as well as silica and magnetite were also detected in all classes. Although neither CaO nor Ca(OH)₂ were identified by XRD analysis, Ca-Al-Fe oxide, Mg-Cr oxide, periclase as well as calcite, showed higher peak intensities in class D. Raman spectroscopy (results not shown here) confirmed some of the results of elemental and XRD analyses, revealing the presence of Si, Fe and Al minerals including alumina, magnetite, olivine and also indicated calcite presence in all fractions, but was not able to detect calcium silicate or oxide phases.

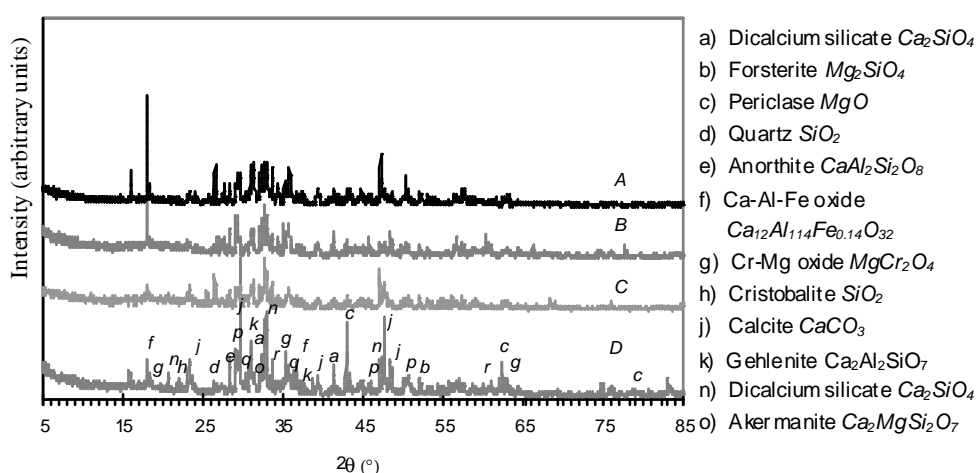


Figure 2: XRD patterns for the different particle size fractions of slag

The main results of the accelerated carbonation tests are reported in Figure 3. Carbonation kinetics was quite fast, reaching completion in 2–4 h depending on operational conditions. In Figures 3a and 3b the influence of CO₂ pressure and temperature on the carbonation kinetics for class D are shown; similar trends were also found for the other fractions, although with significantly lower CO₂ uptakes. Pressure did not appear to affect either the CO₂ uptake or the reaction kinetics, in agreement with results obtained under similar operating conditions for other types of combustion residues.^{26,36)} Temperature, other than grain size, was the parameter that mostly affected the slag reactivity towards CO₂, leading to CO₂ uptakes of just below 13 wt% in 2 h. This effect was ascribed to the enhancement of silicate dissolution, indicated as an important factor in slurry-phase steel slag carbonation.¹⁹⁾ The L/S ratio was also an important parameter for aqueous phase carbonation,^{16,19)} with the highest CO₂ uptakes being achieved at L/S ratios of 0.3–0.4 l/kg (Figure 3c). As found by other studies, CO₂ uptake varied considerably with particle size (Figure 3d); since no remarkable difference in elemental and mineralogical composition was detected, except for a slight increase of Ca and Mg oxides content in class D, the reduced surface area of the slag with increasing particle size was considered as the main mechanism behind the decrease in slag reactivity towards CO₂. This hypothesis was confirmed by results of accelerated carbonation tests on milled ($d < 0.425$ mm) class A slag, which displayed CO₂ uptakes similar to class C ($0.105 < d < 0.177$ mm), indicating that intensive milling could contribute to enhancing the carbonation yield considerably.

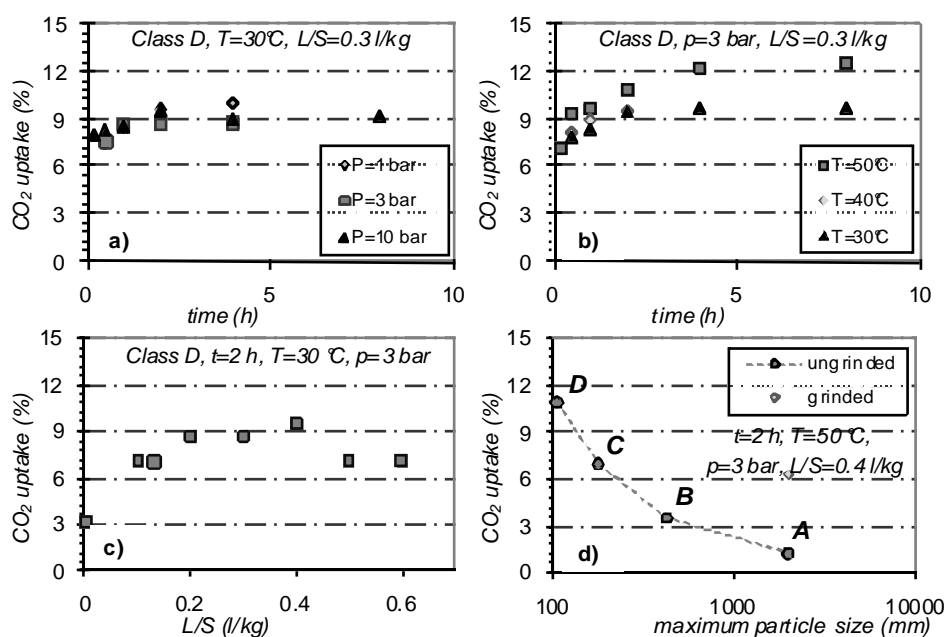


Figure 3: CO₂ uptake vs. (a) pressure; (b) temperature; (c) L/S ratio; (d) particle size

The carbonated slag, particularly for $L/S > 0.2$ l/kg and $T = 50^\circ\text{C}$, exhibited a compact, hardened cement-like structure, suggesting that through accelerated carbonation slag aggregates with appreciable mechanical properties may be produced.

The XRD patterns of carbonated samples (Figure 4) indicated the disappearance of periclase, a significant reduction in the peak intensities for Mg-Cr and Ca-Al-Fe oxides, as well as a reduction of silicate phases such as dicalciumsilicate, anorthite and cuspidine, accompanied by a significant increase in peak intensities for calcite and evidence of dolomite formation; only Mg-containing carbonates were not identified. Quartz and cristobalite peaks were not modified after carbonation. These results are in good agreement with previous studies³⁷⁾ that evidenced the increase in calcite peaks, the decrease of periclase, portlandite and partially also of dicalciumsilicate, while an unmodified pattern for merwinite, akermanite and silica.

The results of the EN 12457-2 leaching test after carbonation (see Table 2) revealed a decrease in the natural pH for all the carbonated samples, which was more pronounced (by almost 2 units) for class D. The only compounds whose leaching appeared to be significantly modified by the treatment were Ca and Si. Ca concentrations in the eluates were considerably reduced, by up to one order of magnitude, for all size fractions, indicating the formation of less soluble phases, such as calcite, than those making up the original slag. Unlike Ca, Si concentrations significantly increased in the eluates of all carbonated samples, except for class D, indicating that indeed part of the silicates reacted during carbonation, releasing more soluble silica phases. These results are in good agreement with previous findings³⁸⁾ on steel slag carbonated under similar

operating conditions. Cr release appeared to be slightly reduced only for class B and C samples, although remaining higher than the regulatory limit of 0.5 mg/l for inert waste disposal.

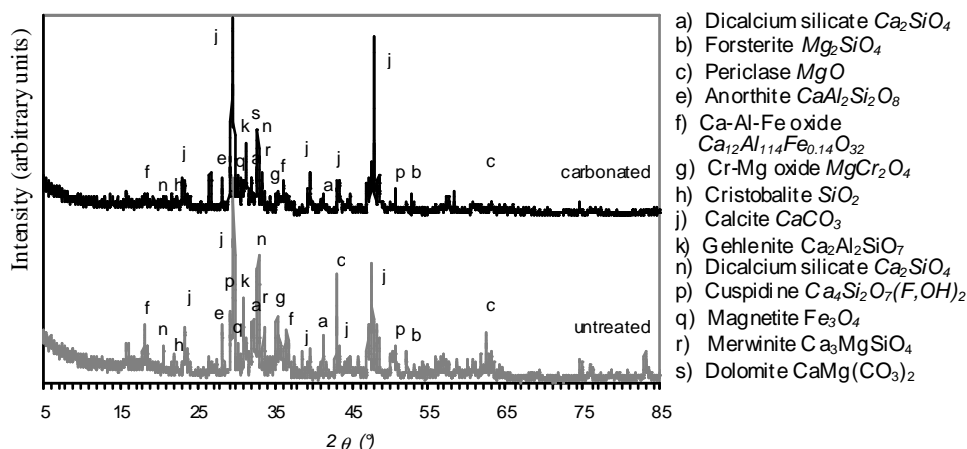


Figure 4: XRD patterns for the untreated and carbonated (2 h, 0.4 l/kg, 50°C and 3 bar) class D fraction

As for the ANC behaviour of SSS, both the untreated and the carbonated class D samples showed a significant (~10 meq/g) acid buffering capacity in the pH range 8–10. The buffering capacity of carbonated slag at pH>10 was reduced, owing to the decrease in free oxides, whereas no significant increase in the pH range 7–8, typical of calcite control, could be observed for carbonated SSS compared to untreated samples; this was probably due to the fact that partially reacted silicates buffer in similar pH ranges. Similar results were reported by other authors.³⁷⁾ The pH-dependant leaching of Ca, Mg, Si and Cr for class D, as derived from the ANC test, is reported in Figure 5. The leaching curve for Ca confirmed the results of the EN 12457-2 test, showing a decrease in leachate concentration for pH > 8 due to calcite formation, whereas for Mg a mobilisation effect in the same pH range was observed, which could be due to the formation of hydrated soluble species, indicating that no significant precipitation of Mg carbonates occurred, as observed by other authors.³³⁾ Si leaching as a function of pH did not show significant variations after carbonation, probably owing to the low degree of reactivity of silicate minerals under mild carbonation conditions. The shape of the leaching curve for Cr was not appreciably modified by the carbonation process, likely due to the Cr(III) solubility characteristics.³³⁾

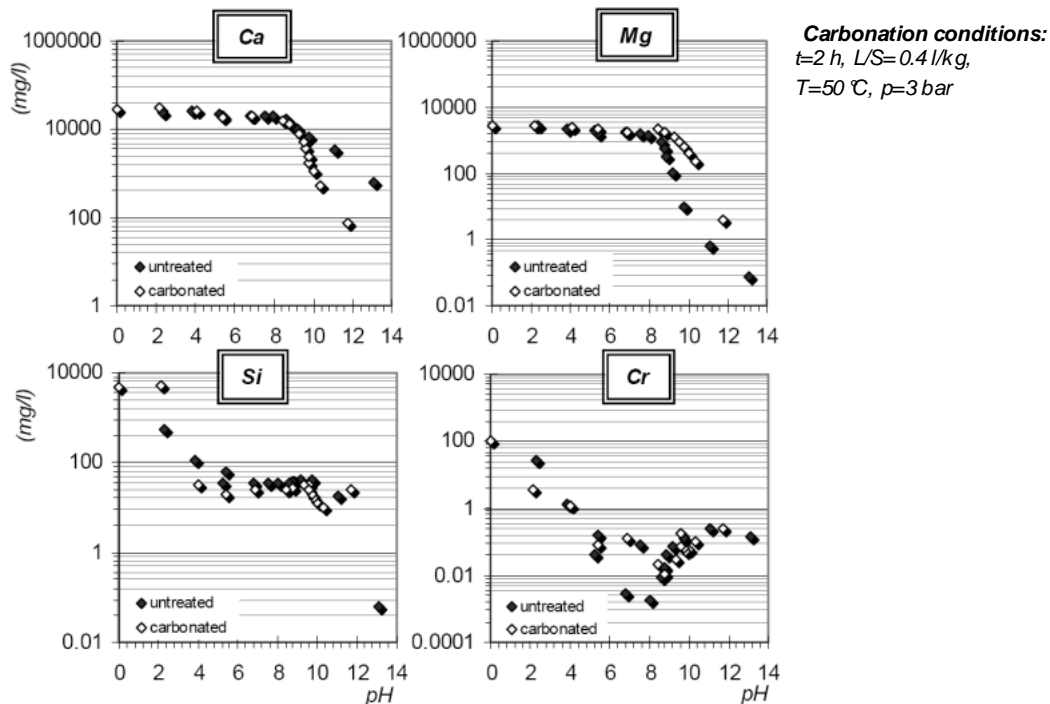


Figure 5: pH-dependant leaching for untreated and carbonated class D fraction

Conclusions

The results of this study indicate that carbonation conducted under mild operating conditions on different particle size fractions of SSS affected several material properties. Chemical and mineralogical characterisation indicated that all size fractions had a high potential for reacting with CO_2 , owing to the high Ca and Mg contents. The parameter that most affected the CO_2 uptake of the slag was found to be grain size, and in particular the specific surface area of the particles. An increase in temperature had also a positive effect. The maximum CO_2 uptake found in this study (13 wt%) was not significantly lower than those reported for slurry-phase steel slag carbonation,¹⁹⁾ however, there is still potential to increase the conversion yield for Ca and Mg reactive species into calcite, which was rather low (~20% for class D), compared to that reported for the above mentioned study. Ongoing tests are assessing the effects of milling and higher operating temperature on slag carbonation yields. Another aspect that needs to be further examined is the ability of accelerated carbonation to enhance the mechanical and structural properties of the slag, which may be an interesting effect with a view to utilisation of the material in engineering applications.

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Session 2

Hot stage slag processing to improve final properties

Mineralogical Influence of Different Cooling Conditions on Leaching Behaviour of Steelmaking Slags

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Abstract

The Swedish steelmaking industry produces large amounts of by-products. In 2006, the total amount of slag produced reached approximately 1.375.000 metric tons, of which 30% was deposited. By controlling and modifying process parameters during slag handling in the liquid state, the physical properties of steel slags can be adequately modified to obtain a high-quality product for external application. Two types of steel slags, BOF (Basic Oxygen Furnace) slag and EAF (Electric Arc Furnace) slag were characterised and modified by semi-rapid cooling in crucibles and rapid cooling by water granulation. The leaching tests showed that water granulation did not prevent leaching of minor elements from the modified slags. The solubility of chromium, molybdenum and vanadium varied in the different modifications, probably due to their presence in different minerals. The reactivity factor, α , was calculated for the BOF and EAF slag. A majority of the elements of interest in the slags became more reactive when cooled rapidly.

Introduction

Large amounts of by-products are produced by the Swedish steelmaking industry each year. In 2006, the total amount of slag produced, reached approximately 1.375.000 tonnes. Only 44%, mostly blast furnace slag, was sold as external products, and approximately 30% was used for landfilling (source: private communication with the steelmaking industry). These figures are very high in comparison to other European countries. In Germany, only 7% of the steel slags produced are dumped, while 93% is used for other applications.³⁾ In Sweden, a number of goals have been formulated in order to obtain a so-called good building environment.⁴⁾ Among these criteria are:

- By 2010, re-used material should represent at least 15% of the aggregates used.
- Landfill waste should be reduced by at least 50% by 2005 compared to 1994.

Due to its strength, durability and chemistry, steel slag could be considered in the field of construction, since the material provides similar properties as granite and flint gravel.³⁾ Using slag in construction would contribute to a reduction in the amount of landfilled waste. The possibility of using slag is limited due to the lack of rules and

guidelines regarding testing, assessment and use of slag in Sweden. The technical and environmental obstacles for not using some slags in construction include:

- Volumetric expansion
- Disintegration
- Leaching of metals.

According to Monaco and Lu,⁵⁾ the volumetric expansion is considered to be associated with the presence of free lime and free periclase in the solidified slag. Free lime and periclase react with moisture, resulting in an expansion due to the formation of hydroxides.⁶⁾

Upon cooling, pure dicalciumsilicate undergoes a phase transformation from β -Ca₂SiO₄ to γ -Ca₂SiO₄ at approximately 500°C. The latter results in a volume expansion of approximately 12 vol%.⁷⁾ The polymorphic transformation of β -Ca₂SiO₄ to γ -Ca₂SiO₄ is known to occur in AOD slag (Argon Oxygen Decarburisation) depending on the cooling rate.⁸⁾ However, that has not been reported for EAF slags.⁹⁾ Thomas and Stephenson¹⁰⁾ believe that impurities in the EAF slag stabilize the metastable β -Ca₂SiO₄ from disintegration.

Very little is reported in the literature regarding the influence of cooling on the properties of slag, especially for steelmaking slags (EAF, BOF). Ground granulated blast-furnace slags (GGBS) are known to possess improved hydration reactivity compared to slowly cooled blast furnace slag, due to the formation of glass.¹¹⁾ The formation of a glassy material depends on both the chemical composition and the cooling conditions. According to Daugherty *et al.*¹²⁾, glass was easier to produce, as the acidity of the slag increased for a series of synthetic slag compositions that was quenched and annealed. Ionescu *et al.*^{13,21)} have shown how water quenching of steel slag results in products with a high content of glassy material. Silicate melts have high viscosity due to long molecule chains, and rearrangement into crystals only takes place slowly. If the cooling is rapid, the slag passes from a liquid state to a solid without development of a crystalline structure.¹⁴⁾ Glasses, such as granulated slags, can be regarded as super-cooled liquids having a very high viscosity. Monaco and Lu⁹⁾ have reported variations in the composition of the wustite-type solid solution as well as a variation in crystal size when cooling differently. Besides glass formation, controlling cooling conditions can be a means of affecting mineral transformation and consequently the solubility of elements like chromium. Chemical compounds containing hexavalent chromium (Cr⁶⁺) are generally considered far more toxic than those containing the trivalent form (Cr³⁺).^{15,16)} According to Lee and Nassarella,¹⁷⁾ Cr⁶⁺ is usually formed at lower temperatures and a rapid cooling reduces the formation by limiting the kinetics of the formation.

The present work was undertaken as a research project within the Minerals and Metals Recycling Research Centre, MiMeR. The major objectives were to investigate how different cooling methods and cooling rates influence the properties of slag products.

Experimental

20–30 kg representative samples of two different steel slags were obtained from steelmaking companies in Sweden:

- A. Basic oxygen furnace slag (BOF slag)
- B. Electric arc furnace slag, high alloyed steel (EAF slag)

The materials, were crushed with a jaw crusher, Retsch BB3, to <30-40 mm before splitting into 1-1.5 kg sub-samples. All slags were modified in two ways for comparison with the original (Figure 1):

1. Re-melting and water-granulation (rapid cooling)
2. Re-melting and cooling in the crucible (semi-rapid cooling)

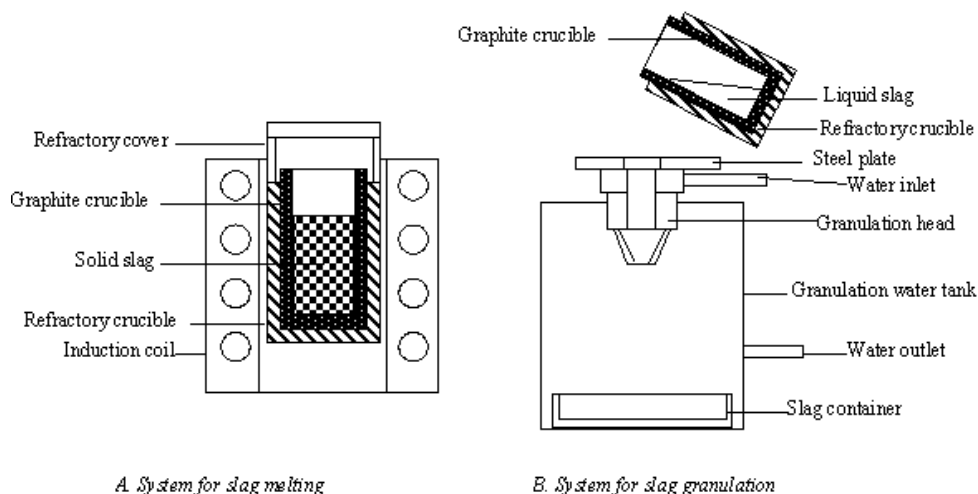


Figure 1: Crucible system (A) and equipment for water granulation (B)

Results

Physical properties

The re-melted slags which were left to cool in the crucibles (semi-rapid cooling) resulted in large pieces that were crushed to <4 mm for leaching tests. The water-granulated material of the BOF and EAF consisted of granular particles, 2-4 mm. Table 1 summarises the compact density, the BET surface and the results from the glass

measuring test of the original and water-granulated slag samples. From this table, it can be seen that the BET surface was reduced substantially in the granular particles, mainly due to the reduction of the amount of fines.

Table 1: The compact density (g/cm^3), the BET-surface (m^2/g) and the glass content (%) in the samples

Sample	Compact density		BET-surface		Glass content	
	Original g/cm^3	Granulated g/cm^3	Original m^2/g	Granulated m^2/g	Original %	Granulated %
<i>BOF - slag</i>	3.53	3.65	2.35	0.21	7	1
<i>EAF - slag</i>	3.25	3.34	2.23	0.17	2	17

Physico-chemical and mineralogical characterisation

Chemical compositions of the two original slags are shown in Table 2. It shows that the content of iron oxides is high in the BOF slag. The chromium content is significantly higher in the EAF slag than in the BOF slag.

Table 2: Chemical composition of the original samples

Samples	%								ppm	
	Fe_2O_3	FeO	Fe met.	Al_2O_3	CaO	MgO	MnO	SiO_2	Cr	V
BOF slag	10.9	10.7	2.3	1.9	45.0	9.6	3.1	11.1	506	14800
EAF-slag	1.0	3.3	0.1	3.7	45.5	5.2	2.0	32.2	32700	310

The solubility of five major elements (Ca, Mg, Fe, Si, Al) in the matrix and of three minor elements (Cr, Mo, V), expressed as mg/kg of the element dissolved, is shown in Table 3. The leaching of silica is increased when cooling rapidly, compared to semi-rapid cooling, while the aluminium leaching is decreased when cooling rapidly. No systematic changes in the minor elements can be seen when cooling differently. The values reported by the laboratory are in many cases low. However, there was good agreement between duplicate samples.

Table 3: Results obtained from leaching of investigated slags in (mg/kg)

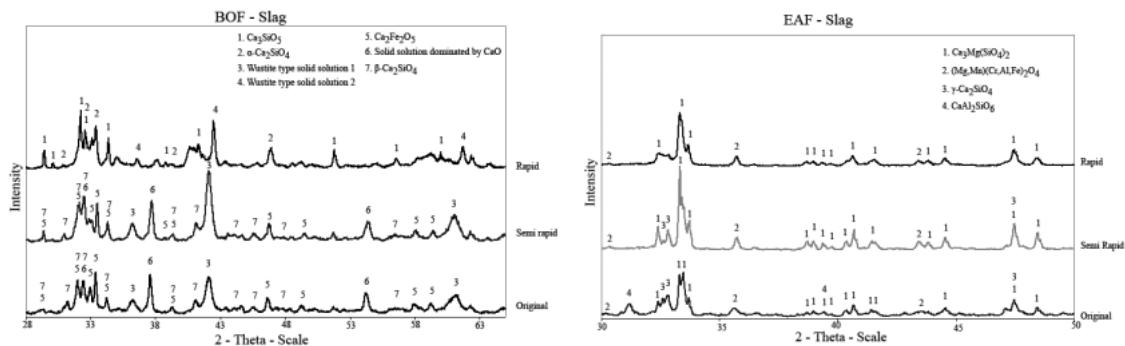
Slag sample	Ca	Mg	Fe	Si	Al	Cr	Mo	V
Limit value ^a						0.5	0.5	
<i>BOF slag</i>								
original ^b	7095	nd	0.14	4.9	2.63	0.03	0.21	0.3
semi rapid cooling ^b	4405	nd	0.07	14.9	19.15	0.01	0.07	0.7
rapid cooling ^b	2070	nd	nd	62.5	1.6	0.04	0.07	7.7
<i>EAF slag</i>								
original ^b	1145	nd	0.04	37.4	139	0.73	3.9	0.3
semi rapid cooling ^b	646.5	2.2	nd	140.5	5.12	0.82	0.11	2.8
rapid cooling ^c	457	4.34	nd	132.2	2.73	0.93	0.07	0.3

nd = not detected

^a = Limit value for inert landfill^[1] b = prEN 12457-2 ^[2] c = prEN 12457-3

X-ray diffraction analyses

All investigated slag samples are basic, M_b ($\text{CaO} + \text{MgO}$)/($\text{SiO}_2 + \text{Al}_2\text{O}_3$) > 1, also known as B_4 , which according to Daugherty *et al.*^[12] results in mainly crystalline slags. The values of M_b are 3.9 and 1.4 for BOF slag and EAF slag, respectively. The comparison of the XRD pattern of the original and the modified slags, shows that all samples, consist largely of crystalline material. The phases present in Figure 2 are those that are likely to be present when also results from e.g. the SEM (Scanning Electron Microscopy) studies are considered.

**Figure 2:** XRD pattern of the investigated slags, with different cooling conditions

Thermodynamic calculations

Thermodynamic calculations in Factsage were conducted for BOF and the EAF slag. The result of the thermodynamic calculation is shown in Figure 3. The calculations are based on the following conditions:

Temperature interval : 25-1800°C
 Pressure: 1 atm, constant

Phases formed in less than 3 wt% were omitted from Figure 3. According to the results given in Figure 3, the first crystalline phase to precipitate from the liquid BOF slag is MgO, followed by the crystallisation of FeO and CaO entering solid solution. Tricalciumsilicate, Ca_3SiO_5 , is the first silicate to crystallise at approximately 1450°C. Below ~1270°C, Ca_3SiO_5 is transformed to α' - Ca_2SiO_4 and CaO. The first phase to precipitate from the liquid EAF slag is magnesiumchromite, which crystallises above 1800°C. In addition, MgCr_2O_4 is further transformed into chromite (FeCr_2O_4) at ~1270°C. Alpha-dicalciumsilicate, α - Ca_2SiO_4 , is the first silicate to form in liquid EAF slag at approximately 1530°C.

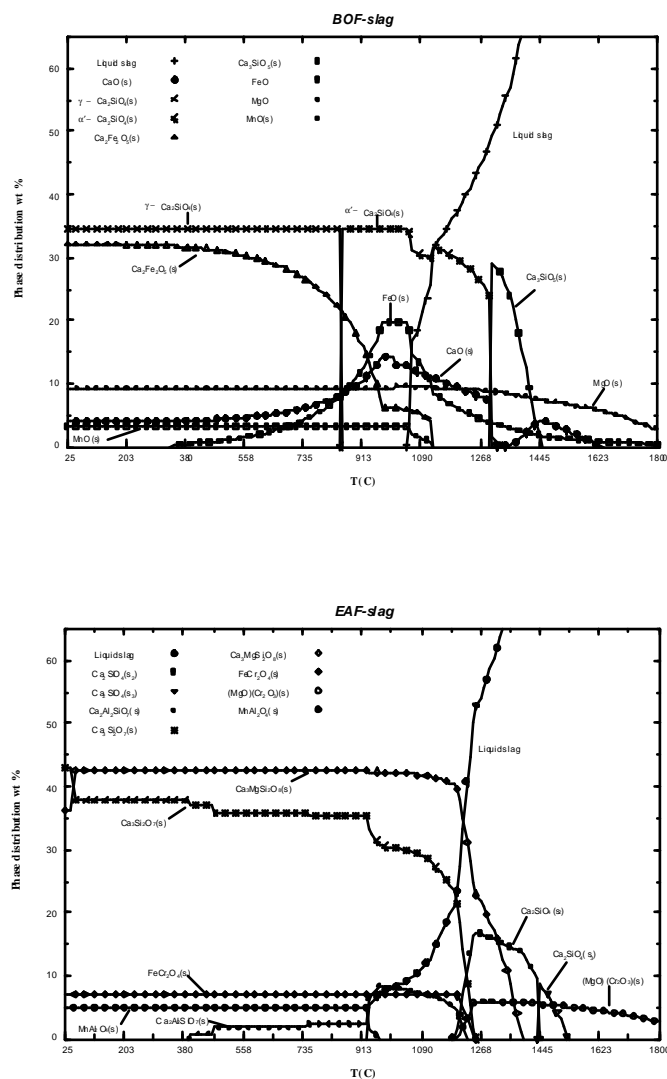


Figure 3: Thermodynamic calculation in Factsage

Discussion

A mineralogical interpretation of the solidification/solubility

The investigations with XRD were complemented with SEM studies in order to evaluate the impact of different cooling methods on the matrix of the slags. According to both the XRD and the SEM analyses of the modified slag, it could be noted that there was a clear difference in particle size distribution due to the different cooling conditions.

BOF slag

The original BOF slag has high specific surface because of a high content of fines and pores compared to the granulated slag. According to the XRD results, Figure 2, the major phase in the original BOF slag is larnite, $\beta\text{-Ca}_2\text{SiO}_4$. With SEM and mapping of selected elements, silicon and calcium were detected in the same phase, agreeing with the finding of larnite as the major phase. Parts with high coexistence of iron, manganese and magnesium were also distinguished with SEM; possibly, the $(\text{Mg,Fe,Mn})\text{O}$ solid solution also found with XRD.

In the semi-rapidly cooled BOF slag, four crystalline phases were identified with XRD. A wustite-type solid solution containing magnesium, iron and manganese $(\text{Mg,Fe,Mn})\text{O}$, β -calciumsilicate ($\beta\text{-Ca}_2\text{SiO}_4$), calciumferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) and a calcium, manganese oxide $(\text{Ca,Mn})\text{O}$ phase. All phases except for the $(\text{Ca,Mn})\text{O}$ were also detected with SEM and mapping, Figure 4, particle 1-3. The $(\text{Mg,Fe,Mn})\text{O}$ is enclosed in the $\beta\text{-Ca}_2\text{SiO}_4$ structure, indicating an early crystallisation, in comparison to $\beta\text{-Ca}_2\text{SiO}_4$ and $\text{Ca}_2\text{Fe}_2\text{O}_5$.

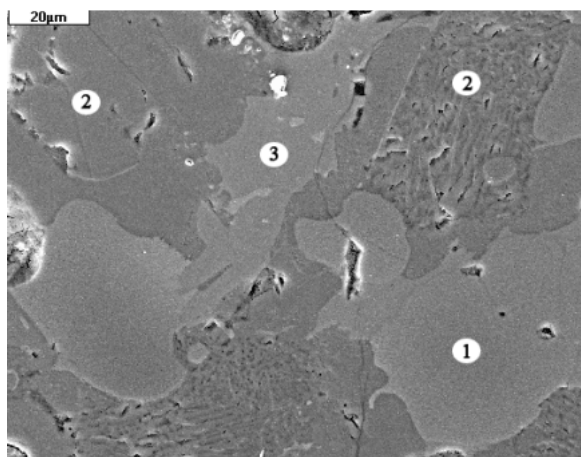


Figure 4: Scanning electron micrograph of the semi-rapidly cooled BOF-slag. (1) $(\text{Mg,Fe,Mn})\text{O}$, (2) Calciumsilicate, (3) Calciumferrite.

In the rapidly cooled BOF slag, three crystalline phases were identified through XRD. A wustite-type solid solution containing magnesium, iron and manganese (Mg,Fe,MnO), tricalciumsilicate and $\alpha\text{-Ca}_2\text{SiO}_4$. These phases were also confirmed by SEM, phase 1-3, Figure 5, where phase 2 is tricalciumsilicate (Ca_3SiO_5) i.e. the euhedral prismatic microphenocrysts, that according to Goldring and Juckes¹⁸⁾ are typical for Ca_3SiO_5 and phase 3, the matrix phase, crystallising last, probably containing the $\alpha\text{-Ca}_2\text{SiO}_4$ seen in XRD. All phases identified in the rapidly cooled BOF slag, agree with the thermodynamic calculation, Figure 3, i.e. indicating that the fast cooling enables the presence of metastable phases, such as Ca_3SiO_5 and $\alpha\text{-Ca}_2\text{SiO}_4$ at lower temperatures. As seen in Figure 2, the composition of the wustite-type solid solution is different when comparing the semi-rapid and the rapidly cooled BOF slag. According to the thermodynamic calculations, Figure 3, MgO is already present as crystals in the liquid slag at 1600°C . The slight change in position, which occurs in the diffractogram, is explained in terms of having a higher concentration of MgO in the wustite-type solid solution. As the slag is cooled rapidly, neither the FeO nor MnO has the same possibility of crystallising and forming a solid solution with MgO , due to its later crystallisation in comparison to MgO , Figure 3. The latter was further confirmed by the SEM instrument. According to semi-quantitative analyses, the solid solution contains 51% MgO , 42% FeO and 7% MnO , in the semi-rapidly cooled slag, while the solid solutions in the rapidly cooled slag was made up of 78% MgO , 16% FeO and 6% MnO .

When a phase can form thermodynamically, the crystal size will depend on the temperature to which the crystals are exposed and the duration of the exposure. There was a significant difference in crystal size between the two modified BOF slags, Figure 4-5. The size of the crystals present in the semi-rapidly cooled slag varied between 40-200 μm , indicating that these minerals have had longer time to grow. In the rapidly cooled BOF slag, the variation in crystal size is more pronounced compared to the semi-rapidly cooled BOF slag. The wustite-type solid solution (phase 1) and the tricalciumsilicate (phase 2), Figure 5, has a crystal size varying between 20-100 μm . The matrix (phase 3), Figure 5, has a much smaller size than the other two phases discussed. The smaller crystal size of this silicate matrix can thus be explained in terms of not having the same time to develop. Based on the thermodynamic calculations, it can be concluded that both the wustite-type solid solution and the tricalciumsilicate were present in the liquid slag at the time the rapid cooling with water was carried out. However, $\alpha\text{-Ca}_2\text{SiO}_4$ is expected to form during rapid cooling with water.

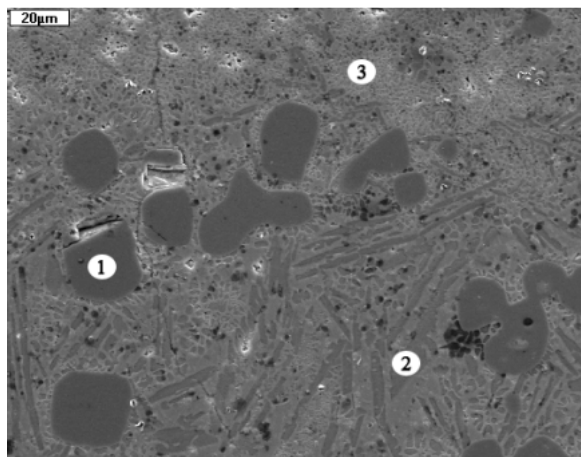


Figure 5: Scanning electron micrograph of the rapidly cooled BOF-slag. (1) (Mg, Fe, Mn) oxide, (2) Calciumsilicate, (3) Matrix containing (Ca, Si, Ti, V, Mn, Fe) oxides.

The leaching of calcium and iron is reduced in the granulated BOF slag, according to Table 3. Iron is present in the matrix, as discussed above, and the leaching is very low in all three slag samples. Calcium, on the other hand, is also present in the major silicate phase, Ca_3SiO_5 . The solubility of silicon is increased in the granulated slag compared to the original. The leaching result shows that the dissolution of the minor elements is not prevented by the rapid cooling procedure, see Table 3. Vanadium is most soluble in the granulated BOF slag, correlating to the silica leaching, indicating a more enhanced leaching from the fine grained silicate matrix.

EAf slag

The XRD graphs of the EAF slag, Figure 2, show that the original and the two modifications contain a large proportion of crystalline phases. In the semi-rapidly cooled EAF slag three crystalline phases were identified with XRD (Figure 2), i.e., a spinel containing magnesium and chromium (magnesiochromite, MgCr_2O_4), calcium magnesium silicate (merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$) and γ -calcium silicate ($\gamma\text{-Ca}_2\text{SiO}_4$). Both merwinite (phase 1) and magnesiochromite (phase 3) were found with SEM as well (Figure 6).

From Figure 6, it can be seen that manganese is present in the solid solution along with chromium and magnesium. Except for the three phases which were found with XRD, an additional phase was observed with SEM and mapping, i.e., a calcium alumina silicate phase (phase 2), see Figure 6. According to the thermodynamic calculation (Figure 3), only one phase of calcium alumina silicate exists in the system, namely $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite). Gehlenite is thermodynamically formed below 1270°C according to the calculations. The later crystallisation of gehlenite agrees well with the texture of the semi-rapidly cooled EAF slag. As seen in Figure 6, both the merwinite and the spinel found have their own specific structures, characterized by sharp edges, while the gehlenite is located between the other two. According to the thermodynamic

calculations (Figure 3), both merwinite and the spinel crystallise earlier than gehlenite, which explains the texture of the semi-rapidly cooled EAF slag.

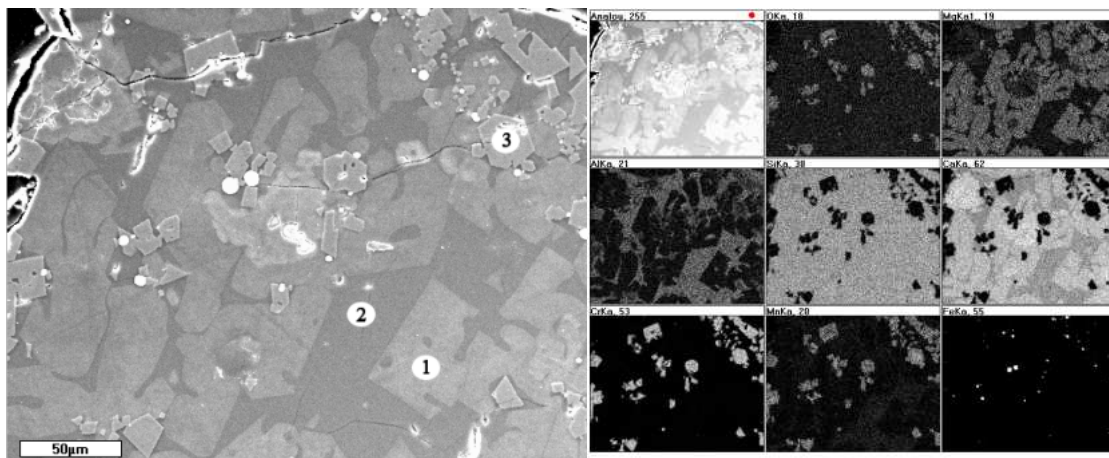


Figure 6: Scanning electron micrograph and accompanied mapping of the semi-rapidly cooled EAF slag. (1) Calcium magnesium silicate, (2) Calcium alumina silicate, (3) Chromium containing spinel.

Two crystalline phases were identified in the rapidly cooled EAF slag with XRD (Figure 2), both similar to those that were found in the semi-rapidly cooled EAF slag, merwinite and the spinel, containing magnesium and chromium. When comparing the diffractogram in Figure 2, a broadening of the peak width can be observed as a result of the rapid cooling with water. Suryanarayana and Grant¹⁹⁾ suggest that this may be caused by a decreased crystallite size.

Furthermore, the differences in crystal size found between the two modified slags are significant (Figures 6-7). The spinel phase has the same size and texture in both materials, while the rest of the phases vary a lot, indicating that the spinels were crystallised already at the time the granulation started, which is also confirmed by the calculations (Figure 3). The large well-defined merwinite and gehlenite crystals which were found in the semi-rapidly cooled slag were no longer present in the rapidly cooled EAF slag. Instead, a mixture of calcium, magnesium, alumina and silica were found: area 2 (phase 2), Figure 7. According to the theory on nucleation and growth, area 2 most likely consists of small merwinite and gehlenite crystals, due to the rapid cooling i.e., the rapid crystallisation.

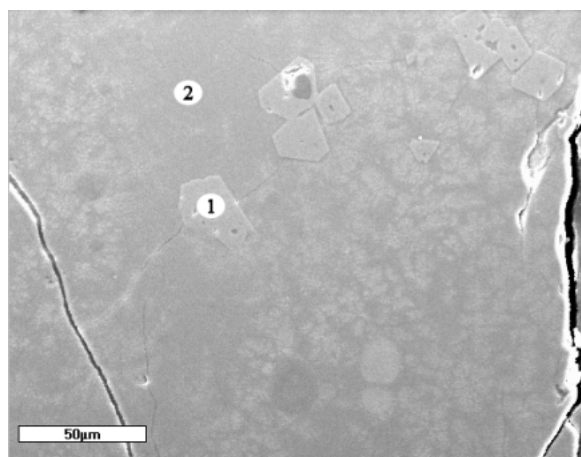


Figure 7: Scanning electron micrograph of rapidly cooled EAF slag. (1) Chromium containing spinel, (2) Complex of (Ca, Al, Si, Mg) oxides

The content of calcium and silicon is high in the EAF slag (Table 2). The solubility of these two major elements, as well as aluminium, iron and magnesium, is shown in Table 3. The leachability is very low and varies in the three modifications. The solubility of aluminium is reduced substantially in the semi-rapidly cooled and the granulated slag, which indicates that one of the matrix-forming phases is stable. On the other hand, the mobility of silica seems to increase when granulating. There does not seem to be any obvious correlation between the solubility of the major and the minor elements. The varying dissolution of the metals chromium, molybdenum and vanadium is more likely a result of the presence in different minerals. The solubility of chromium is very low, 20 ppm of the total chromium content, in all three samples. Vanadium, on the other hand, is most leachable in the semi-rapidly cooled slag.

Reactivity, BOF and EAF slag

The leaching from steel slags is generally characterised as a surface reaction, followed by a solid-solid diffusion process, in order to retain equilibrium in the materials.²⁰⁾ A minimisation of the surface area of the slag is therefore likely to enable a decrease in leachability. Leaching and specific surface data regarding these materials are listed in Table 1 and Table 3. The specific surface area data was unfortunately not measured in relation to the semi-rapidly cooled samples. Anyhow, since the original and semi-rapidly cooled samples were prepared for leaching in the same way (crushing < 4 mm), it is assumed that these materials have a similar specific surface area.

It has earlier been concluded that no distinct changes in the total leachability could be noticed when comparing the semi-rapidly cooled with the rapidly cooled materials. However, a decrease in the specific surface area was noted when the semi-rapidly cooled slag was compared against the rapidly cooled slag. To gain a better understanding of the reactivity with regard to the surface chemistry of the differently

cooled slags, a reactivity factor α was introduced and calculated according to equation (1). The reactivity ratio of the rapidly and semi-rapidly cooled slags is given in Table 4.

$$\alpha = \frac{\text{Leached amount}}{\text{Specific surface area}} = \frac{(\text{mg}) \text{ leached from } (\text{kg}) \text{ dry material } (\text{mg/kg})}{\text{m}^2/\text{kg}} = \text{mg/m}^2 \quad (1)$$

Table 4: The α -ratio of rapid and semi-rapidly cooled slag.

Element	BOF slag			EAF-slag		
	α Semi-rapid cooling	α Rapid cooling	(Rapid)/(Semi) %	α Semi-rapid cooling	α Rapid cooling	(Rapid)/(Semi) %
Ca	1,87E+00	9,86E+00	526%	2,90E-01	2,69E+00	928%
Na	1,87E-03	2,89E-02	1543%	1,09E-03	3,09E-02	2824%
S	4,62E-03	1,06E-01	2305%	2,55E-03	1,52E-02	596%
Si	6,34E-03	2,98E-01	4694%	6,30E-02	7,78E-01	1235%
Al	8,15E-03	7,76E-03	95%	2,30E-03	1,61E-02	701%
Ba	1,75E-04	8,93E-04	510%	2,67E-04	4,05E-04	151%
Cr	3,29E-06	1,74E-04	5284%	3,68E-04	5,50E-03	1494%
Mn	4,23E-05	3,99E-05	94%	6,26E-06	5,23E-05	835%
Mo	2,79E-05	3,11E-04	1117%	4,82E-05	3,84E-04	797%
V	2,98E-04	3,67E-02	12317%	1,24E-03	1,79E-03	144%

As seen in Table 4, there are important differences in reactivity due to the different cooling conditions. Almost all elements become more reactive if treated with rapid cooling. The reactivity for silica is increased by ~ 4700% and ~ 1200%, respectively, and for chromium ~ 5300% and ~ 1500%, respectively, for the BOF and EAF slag. Unlike the blast furnace slag, which also becomes more reactive when cooled rapidly, due to the high content of amorphous phases, both the quenched BOF and EAF slag have a low content of glass. Instead, two possible explanations for the increase in reactivity are the presence of metastable phases and the increase in small crystals on the surface due to the rapid cooling with water.

Table 5: Factors potentially affecting increased reactivity

Oxidation	During the rapid cooling with water, oxidation on the surfaces may occur, and thereby the formation of soluble phases.
Surface structure	Fast cooling will result in an abrasive surface, due to the presence of smaller grains at the surface. An abrasive surface tends to be more reactive than a plane surface, due to the increase in vapour pressure that occurs over a convex surface.
Increased amount of grain boundary	Fast cooling will result in more grain boundaries due to the increase of small crystals in the material. Diffusion reactions are known to occur easier and faster along these boundaries.
Metastable phases	Increased solubility with water.

Concluding discussion

Two different types of steel slags have been modified using different cooling techniques. The influence of the cooling conditions were then evaluated based on the final mineralogy of the slags. Variations in crystal size, phase distribution, phase composition, glass content as well as reactivity have been determined. The increased reactivity when cooling rapidly may depend of several factors, listed in Table 5.

It can be concluded that in the search for new and better slag products, both for metallurgical applications and other uses, it is vital to consider the influence of cooling. It can also be concluded that all slags behave differently, depending on their chemical composition, and must be treated individually.

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Stainless Steel Slag Valorisation: on Volume Stability and Disintegration

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Abstract

Together with environmental compatibility and mechanical strength, volume stability is often stated as a key requirement for stainless steel slag valorisation. However, the term volume stability covers more than one physical phenomenon. In this article, the authors discuss the different aspects of the volume stability, pin-point the underlying physical causes for the volume instability and provide a framework to differentiate between them. Possible solutions to cope with volume instability in its broadest sense are listed and discussed as well.

Introduction

Annual worldwide stainless steel production totalled nearly 29 Mt in 2007.¹⁾ The vast majority is produced using an electrical arc furnace (EAF) to melt a raw material mixture containing stainless steel scrap, carbon steel scrap, ferroalloys (FeNi and FeCr) and fluxes. The molten steel is then refined using convertor, Argon Oxygen Decarburisation (AOD) or Vacuum Oxygen Decarburisation (VOD) processes, before being cast. One of the major by-products of the stainless steel production process is slowly cooled and, therefore, crystalline oxidic slag. This slag has CaO, SiO₂ and MgO as its main constituents. Smaller fractions of Al₂O₃, FeO_x and CrO_x are typically present as well. The slag volume amounts to 200 to 300 kg of slag per metric tonne of steel, with about two thirds coming from the refining process and one third from the EAF process.

In 2007, Belgian stainless steel makers produced over 1.5 Mt of crude steel or over 5% of the global production. Correspondingly, nearly 400 thousand metric tonnes of stainless slag was generated.¹⁾ To avoid landfilling, these slags are processed into a valuable secondary resource for the construction industry. The typical application is as a coarse aggregate for asphalt roads or concrete, as Belgian governmental legislation only allows to use stainless steel slags as an aggregate within monolithic applications, due to

environmental considerations. For these applications, grain size distribution, mechanical strength and long-term volume stability are crucial.

During the past few years, the authors of this article have supported the different Belgian stainless steel melt shops with their efforts¹⁻⁵⁾ to improve the ‘volume stability’ of their slags and have reviewed the publically available literature on the topic.⁶⁾ It was noticed that ‘volume stability’ is actually affected by multiple physical phenomena, all of which have different consequences towards the slag quality. To clarify the term ‘volume stability’, the authors discuss its different aspects, pin-point the underlying physical causes for the volume instability and provide a framework to differentiate between them. Possible solutions to cope with volume instability in its broadest sense are listed and discussed as well. The aim of this text is to provide some of the key elements of a pragmatic approach to the issue of stainless steel slag volume stability .

The term volume stability

For the end-user of the slag, *i.e.* the construction industry, volume stability means that the slag particles to be used as aggregates maintain their volume on a long term. If not, *i.e.* when the particles would shrink or swell, the integrity of the concrete or asphalt would be compromised. This is the narrowest definition of volume stability.

For steelmakers, however, the amount of coarse slag particles – as opposed to fine particles – is highly relevant as well, as the coarse fraction is the most valuable for the construction industry. For them, volume stability also includes that the slag does not disintegrate during the solidification and processing of the slag. This is the broader definition of the term.

Table 1: Potential causes of volume instability

Cause	Physics	Distinguishable features
C ₂ S	12% volume expansion during the β to γ phase-transformation of C ₂ S	- Occurs during cooling - Results in very fine slag (< 2 mm)
Free CaO/MgO	Hydration to Ca(OH) ₂ /Mg(OH) ₂	- Occurs after cooling (days to weeks for CaO, months for MgO) - Results in localised cracks
Thermal shrinkage	Steep thermal gradients due to low thermal conductivity lead to high mechanical stresses	- Occurs during cooling - Results in a medium sized slag (2-20 mm)

Physical causes for volume instability

Several physical phenomena affect the volume stability of the slag in its broadest sense, including hydration of free lime or magnesia, the expansive β to γ phase transformation of dicalciumsilicate ($2\text{CaO} \cdot \text{SiO}_2$ or C_2S) and thermal shrinkage.

Hydration of free CaO/MgO

Lime and magnesia are two of the main constituents of stainless steel slags. Potentially, free CaO or MgO are present in the slag microstructure after cooling. This presence can cause a long term volume instability of the slag particles, as both compounds tend to react with water in a humid environment to form, respectively, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. Both these hydration reactions cause a volume expansion or ‘swelling’, which can lead to severe valorisation issues for the construction industry, as explained earlier. Typical features to recognise this type of volume instability are the macroscopic presence of free CaO/MgO ‘pits’ in the slag, the delayed volume instability (weeks to months after the initial slag solidification) and the localised cracks (where the pits are located).

C_2S phase transformation

The presence of C_2S as a mineral in the slag microstructure can drive the disintegration of the slag into a very fine powder with particle sizes typically smaller than $100\text{ }\mu\text{m}$. This mineral undergoes several polymorphic transformations upon cooling (Figure 1), of which the β to γ transformation is accompanied by a volume expansion of about 12%.⁷⁾ This leads to high internal stresses and finally causes the slag to self-pulverise. Macroscopically, one observes that during the initial stage of cooling at the slag yard, slag pieces of several centimetres in diameter and more are formed. However, during further cooling, the pieces suddenly self-pulverise into a fine powder. It is stressed that this disintegration occurs during cooling, making it clearly distinctive from swelling of the slag after cooling due to CaO and/or MgO hydration discussed earlier.

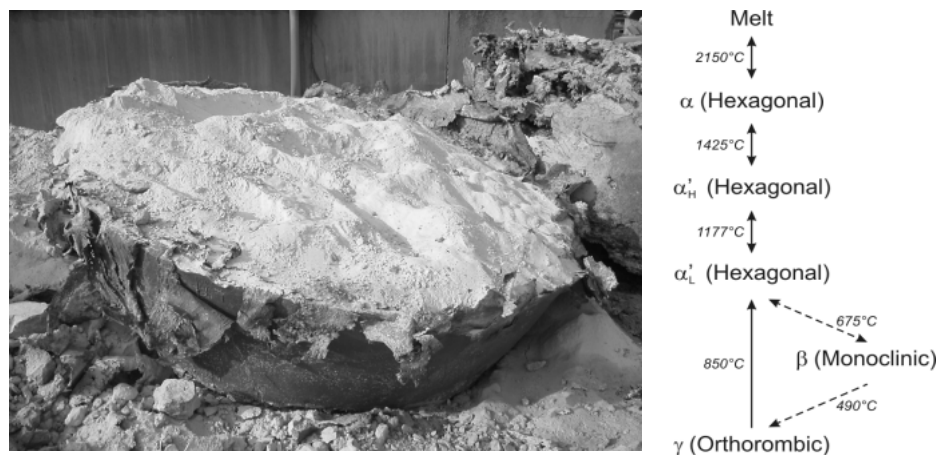


Figure 1: C_2S driven disintegration leads to a very fine slag

Thermal shrinkage

Apart from the two causes listed above, which have been frequently discussed in the scientific literature (see e.g. review paper by Durinck *et al.*⁶⁾), observations during industrial practice led the authors to believe that differential thermal shrinkage during cooling of the slag also affects the slag grain size distribution after cooling. Hence, this should be included in the broader concept of volume stability. When the slag is cooled in subsequent layers in a slag bunker, steep gradients in temperature exist within one slag layer, due to the low thermal conductivity of oxidic slags. The accompanying differential thermal shrinkages lead to mechanical stresses with the slag, causing the slag to break in small pieces. Just as C_2S driven disintegration, this phenomenon occurs during cooling and affects the grain size distribution of the cooled slag in the steel works. However, the slag particles are typically not as fine as with C_2S driven disintegration. In the case of thermal shrinkage driven fines, one can refer to a grain size distribution between 2 and 20 mm.

Potential industrial measures

In the following paragraphs, a number of industrial measures to control the physical phenomena and, consequently, the volume stability of stainless steel slags are discussed. Although the list should contain the most important techniques, it is not claimed to be exhaustive. Rather, the discussion should illustrate the importance of an appropriate slag processing for the properties of a slag product.

Hydration of free CaO/MgO

The common way to ensure the long term volume stability of the slag particles to the construction industry is to weather them for an extended period of time (over 6 months) in environmental conditions in order to complete the hydration reactions prior to shipping the slag to the end-user. However, actions can also be taken to actually prevent any presence of free CaO/MgO in the slag. As free CaO/MgO is often present due to the incomplete dissolution of lime or doloma additions to the slag during the metallurgical process, one should optimise the kinetic conditions of the dissolution reaction. This implies the steady addition of fine-grained lime or doloma to a turbulent system. Note that this can enable lowering the lime or doloma consumption without compromising the steelmaking process (e.g. the requirement of a large CaO content for the sake of desulphurisation). If the CaO does not dissolve into the slag it does not directly contribute to desulphurisation anyway.

On the other hand, if the presence of, particularly, free MgO is caused by exceeding (even) its high-temperature thermodynamic solubility in the slag (e.g. entering the $L + C_2S + MgO$ region of the CaO-MgO-SiO₂ phase diagram, Figure 2), one can adapt the target slag composition (lower MgO level and/or lower C/S ratio). A practical option is

to lower the level of doloma additions, which can be especially relevant during the AOD or VOD process. In this way one avoids entering the $L + C_2S + MgO$ region already at high temperature. Again, the chemistry of the slag remains unchanged by changing a situation of oversaturation to (near) saturation of MgO. This measure is a *condition sine qua non* for avoiding free MgO after slag cooling. In practice, MgO can also precipitate from the slag during the slow cooling procedure at the slag yard. Theoretically, it can be calculated in which areas MgO can be present as a stable phase (assuming thermodynamic equilibrium and thus also infinitely slow cooling). Figure 3 shows the FactSage calculations for the ternary CaO-MgO-SiO₂ system (assuming no further reactions take place below 1000°C). From this it can be seen that free MgO can be completely avoided when the SiO₂ level in the slag is above 33 mole%, which corresponds to approximately 37 wt% SiO₂ for slags with 10 to 15 wt% MgO. If such basicities are too low for metallurgical reasons (during the AOD or VOD process), a practical possibility is to acidify the slag composition, subsequent to the slag/steel separation by, for example, adding SiO₂ sources such as waste glass or sand (see Figure 4) in a separate processing unit.⁸⁾ In the case of stainless steel slags an additional heat source, such as ferrosilicon, would also be required.

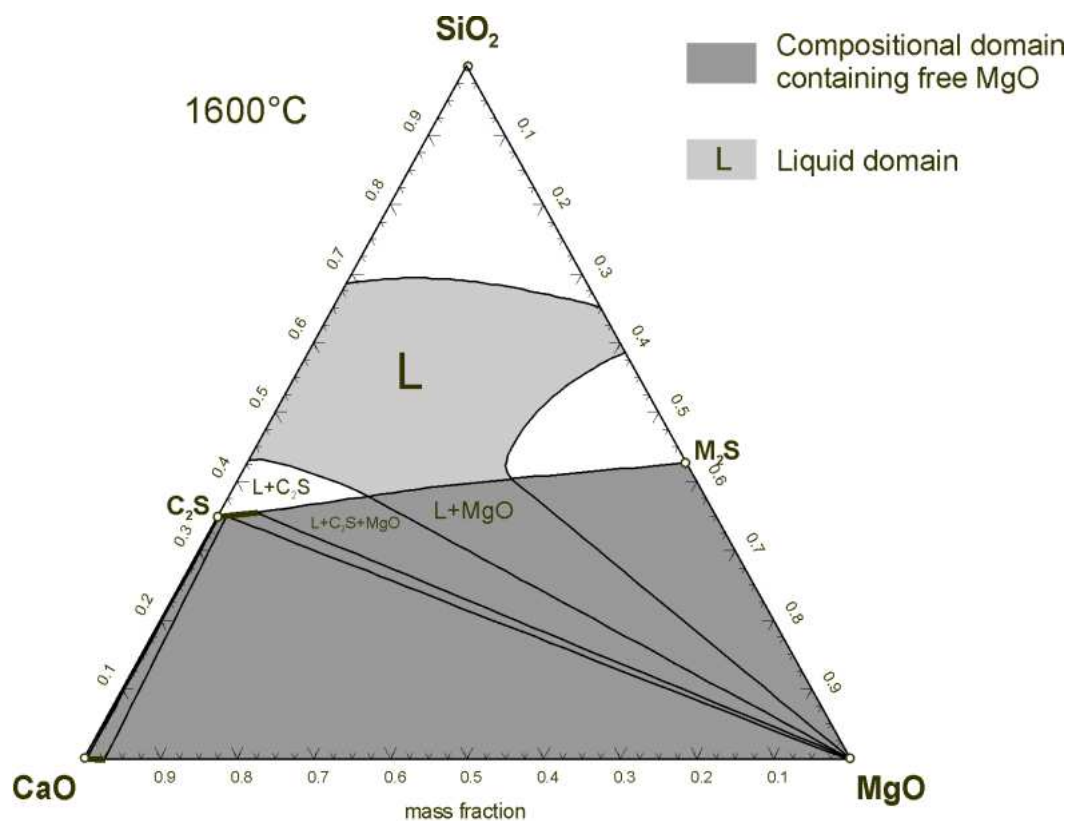


Figure 2: Isothermal section at 1600°C of the CaO-MgO-SiO₂ system showing the various regions.

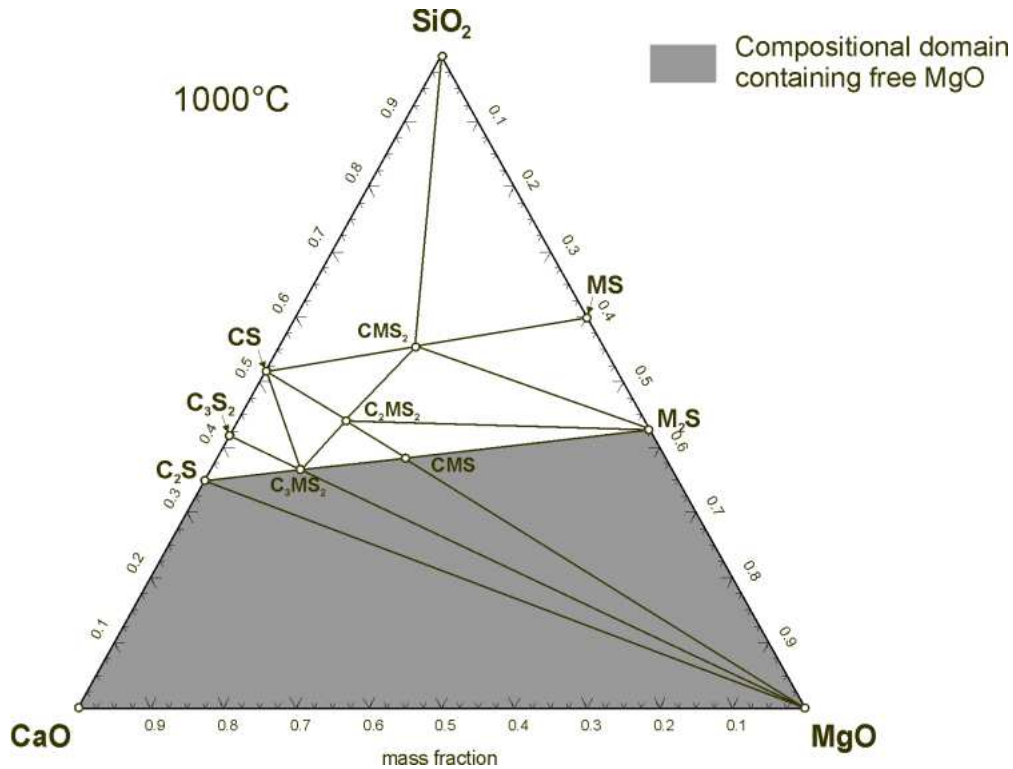


Figure 3: Calculated phase diagram for the phase constitution at room temperature of the CaO-MgO-SiO₂ system. The presence of CaF₂ and other slag components will obviously complicate the real industrial situation.

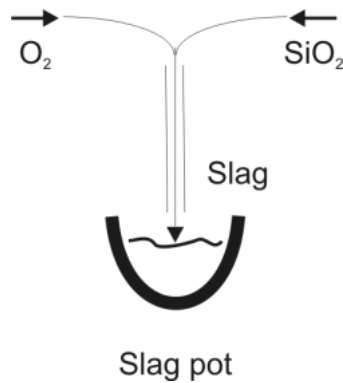


Figure 4: Kuehn *et al.*⁸⁾ developed a process for dissolving a large quantity of SiO₂ (~10 wt%) in carbon steelmaking slags. By co-injecting oxygen, the slag is stirred and FeO in the slag is oxidized to Fe₂O₃, generating the required heat to dissolve the SiO₂. The process is currently operational at ThyssenKrupp Duisburg and ArcelorMittal Gent.

Expansive β to γ phase transformation

The potential treatments can be divided in two main groups, namely preventing the expansive transformation of the mineral to occur or outright avoiding the presence of the mineral in the first place.

The option of inhibiting the β to γ transformation of C_2S was first elaborated in 1986 by Seki and co-workers,⁹⁾ who developed a borate based stabiliser for stainless steel decarburisation slag. At the time, it was already known that borates stabilise the higher temperature polymorphs of pure C_2S to ambient temperatures by forming a solid solution. Seki proved that by adding borates to the high temperature slag, C_2S grains in the cooled slag can also be stabilised. The addition of only 0.2 wt% of B_2O_3 was sufficient to avoid the disintegration of a slag with 51 wt% CaO, 33 wt% SiO_2 and 11 wt% MgO (see e.g. Figure 5).³⁾ As borates increase steel hardness and may lead to hot tearing during rolling or forging, they need to be added to the slag after slag/metal separation to avoid boron pick-up by the steel. Fortunately, the required level is so low that the heat content of the slag is sufficient to melt and dissolve the stabiliser. The treated slag product can be valorised as an aggregate for construction applications. Because of its effectiveness and simplicity, borate stabilisation of air-cooled slags is widely implemented in industrial practice. This solution leads to an additional cost of 1 to 2 € per ton of stainless steel at the current price levels of stabilisers (~600 € per ton of $Na_2B_4O_7$). It must be remarked that, recently, especially in Japan,¹⁰⁾ concerns have risen about the health effects of boron leaching from treated slags. Although boron is an essential trace element for humans, chronic exposure to higher levels can lead to loss of appetite, nausea and decreased sexual activity. The World Health Organisation considers 0.5 mg/l to be a tolerable level of boron in drinking water.¹¹⁾ No studies on the actual boron leaching from slags, however, have been found. Leaching tests on coal ashes indicate that a significant amount of the boron present leaches.

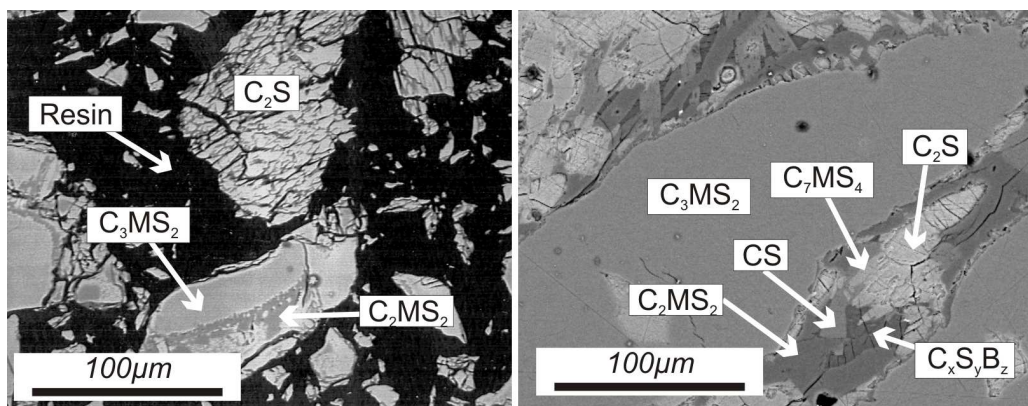


Figure 5: Effect of B_2O_3 additions to a C_2S containing slag. Left: The untreated slag contains fractured γ - C_2S grains and disintegrates during cooling. Right: The treated slag contains stable β - C_2S and did not disintegrate.³⁾

Borate additions are not the single way to avoid the expansive transformation of C_2S and the associated slag disintegration of the slag. A first alternative is to incorporate other ions than B^{3+} in the C_2S crystal, which also exhibit a stabilising effect on β - C_2S . The crystallographic coordination number, the ionic radius and the ionic valence of the doping ion all affect the deformation of the C_2S crystal and, as a consequence, of their stabilisation. Based on this knowledge, the effect of phosphate additions to disintegrating stainless steelmaking slags was investigated. Satisfactory stabilisation was obtained,¹²⁾ but compared to borate additions a significantly larger amount of phosphates (~ 2 wt%) is required to avoid disintegration.

Alternatively, slag disintegration can be averted by outright avoiding the presence of C_2S by modifying the slag composition (*cf.* previous paragraph). Already in 1942, compositional limits were defined for disintegrating slags,¹³⁾ based on the stability field of C_2S in the CaO - MgO - SiO_2 - Al_2O_3 system, with an adjustment for the sulphur content (S) in the slag:

$$CaO + 0.8 MgO \leq 1.20 SiO_2 + 0.39 Al_2O_3 + 1.75 S \quad (1)$$

$$CaO \leq 0.93 SiO_2 + 0.55 Al_2O_3 + 1.75 S \quad (2)$$

with the compounds referring to their respective weight fractions. However, in many cases, slags that meet these conditions do not have the appropriate high temperature metallurgical functionality. In stainless steelmaking, C_2S free, low basicity slags cause rapid refractory degradation and low chromium yields. To avoid making such compromises towards process and metal quality, the slag composition must be adjusted after slag/metal separation. Adding a relatively large amount of silica seems to be the best way to avoid C_2S precipitation. This was proven on a laboratory scale by Sakamoto,¹⁴⁾ who stabilised a stainless steel decarburisation slag with 12 wt% of waste glass, containing 70-75 wt% SiO_2 . The cost of these additions would be far lower than that of the commonly used borate additions. However, an additional slag treatment process as described in Figure 4 is required to extrapolate this method of dissolving large amounts of SiO_2 to an industrial environment.

Apart from the two routes discussed above, it is also known that the phase stability of C_2S is affected by physical aspects, such as the size of the C_2S grains, the cooling rate during formation and the mechanical loads. However, none of these have been translated into industrial treatments (yet).

Thermal shrinkage

Scientific studies towards the effects of the cooling rate on the grain size distribution of stainless steel slags have focussed on the C_2S phase transformation. Indeed, quenching stabilises the β - C_2S grains and prevents the disintegration of the slag into a fine powder. Other effects on the cooling rate have not been studied in-depth. Nevertheless, industrial

trials by Erdmann *et al.*¹⁵⁾ suggest that slow cooling, *i.e.* slag pot cooling during several days, leads to a denser and coarser slag than the commonly used slag pit cooling (Figure 6). Similar trials performed on AOD slags also seem to corroborate that the level of fines – linked to thermal shrinkage – can be mitigated through very slow cooling in slag pots. However, at the moment it is still unclear which specific phenomena cause this improvement. Currently these trials are being investigated in a far more detailed way, looking at both mineralogical changes and the porosity distribution in the different areas of the slag pot. If successful, this slag pot cooling treatment will still need to be extrapolated to a continuous procedure for all AOD or VOD slags. One possibility here would be to create smaller slag bunkers so that the slags can be cooled down in the slag yard in thick rather than thin layers as is currently the general practice. More research and industrial trials are clearly required here.



Figure 6: Large and dense slag blocks for waterway embankments produced by the slow slag pot cooling¹⁵⁾

Conclusion

Valorisation of stainless steel slags can be hampered by a lack of environmental compatibility (*e.g.* high chromium leaching), poor mechanical properties and/or volume instability. The present paper looked at the third issue, which is especially relevant for the more basic AOD and VOD slags. It was shown that the term volume stability covers more than one physical phenomenon, namely fines formation due to free lime and/or magnesia hydration, C_2S driven disintegration and, less documented in literature, thermal shrinkage. In this article, the authors discussed the different aspects of these volume stability problems, pin-pointed the underlying physical causes and provided a framework to differentiate between them. Possible solutions to cope with volume

instability in its broadest sense were listed and discussed. This corroborates that valorisation of AOD and VOD stainless steel slags (as aggregates in shaped construction applications) should not cause any problems any more in the future. Nevertheless, the challenge for the future lies in finding even higher value applications and/or energy recovery from these slags.

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Modification of Stainless Steel Refining Slag through Mixing with Nonferrous Smelting Slag

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Abstract

In Japan, stainless steelmaking technology can be divided into BF-BOF (blast furnace-basic oxygen furnace), SR-BOF (smelting reduction-basic oxygen furnace) and EF (electric arc furnace) processes. Although some slag treatment methods have been reported, the main problems for valorisation are dusting, volume expansion, and leaching of fluorine. On the other hand, by the reduction treatment with addition of Si or Al, the problem of Cr^{6+} is not serious. To prevent dusting, we have proposed a new technology in which the nonferrous smelting slag is mixed with stainless steel slag. Fundamental experiments showed that a mixing ratio of nonferrous slag to total slag higher than 0.2 prevented dusting and produced granular slag.

Introduction

In the stainless steelmaking process, a large amount of slag is generated from EF, argon oxygen decarburisation (AOD), and vacuum oxygen decarburisation (VOD) processes. In general, stainless steel slag has harmful characteristics, including dusting, volume expansion, Cr^{6+} , and fluorine leaching. For this reason, compared with the slag generated by the steelmaking process for plain carbon steel, stainless steel refining slag is difficult to reuse. The first half of this paper summarises the stainless steel refining process in Japan and the characteristics of the slag. To prevent dusting, we have proposed a new technology that uses nonferrous smelting slag. The last half of the paper shows the fundamental results of this modification treatment.

Stainless steelmaking process and slag in Japan

Characteristics of stainless steelmaking technology

In Japan, stainless steelmaking technology can be divided into BF-BOF (blast furnace-basic oxygen furnace), SR-BOF (smelting reduction-basic oxygen furnace) and EF (electric arc furnace) processes (Figure 1). In the BF-BOF process, dephosphorised hot metal is charged into a BOF and ferro-chromium alloy is added during decarburisation. This process is used at Nippon Steel.¹⁾ The SR-BOF process was invented by JFE steel.²⁾ In this process, dephosphorised hot metal is charged into a smelting reduction

furnace, and chromium ore and carbonaceous materials are added. After the smelting reduction, decarburisation is carried out in a BOF. For both processes, ferric stainless steel is produced, and VOD is mainly used as a secondary refining process. On the other hand, to produce austenitic stainless steel, EF is used. Subsequent to EF, BOF or AOD is applied for decarburisation. The EF-BOF process is used at Nisshin Steel, and the EF-AOD process is used at Nippon Steel and Sumikin Stainless Steel (NSSC), Daido Steel, *etc.*

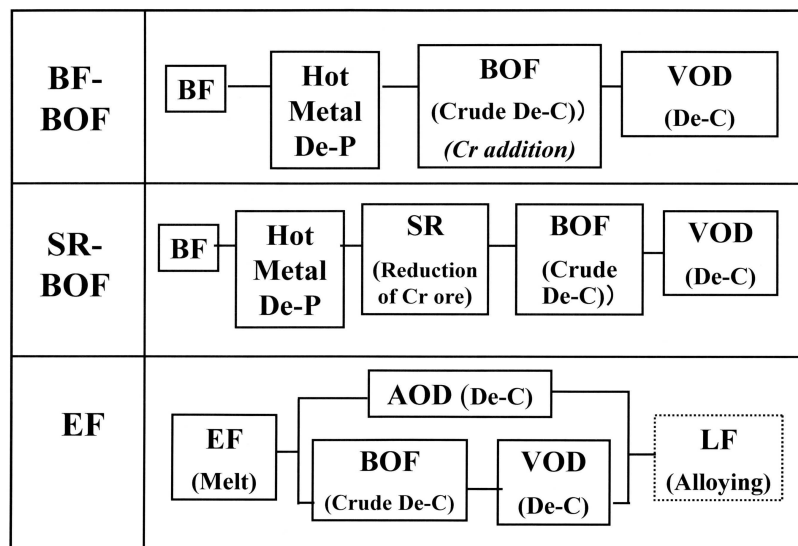


Figure 1: Stainless steelmaking processes in Japan

The estimated amount of slag and composition from each process is shown in Table 1. By reduction treatment after the decarburisation with the addition of Si or Al, the problem of Cr^{6+} is not serious. The main problems for slag valorisation are dusting, volume expansion, and leaching of fluorine.

Table 1: Typical composition and unit generation of stainless steel slag

Process	Composition (mass%)					kg/t
	Cr_2O_3	CaO	SiO_2	MgO	Al_2O_3	
EF	3	41	29	8	10	80
AOD	1	50	30	11	3	90
BOF	3	46	33	10	3	180
SR	1	23	20	30	35	250

Some slag treatment methods have been reported. At JFE Steel, dust from SR, and slag from BOF and VOD are charged into a coke bed type reduction furnace, called a stainless advanced reactor (STAR³⁾) and the slag composition is controlled to avoid dusting and volume expansion. At Daido Steel, dust and dusting slag are melted by a burner to control the composition, called a Daido special method of dust slag melting

technique (DSM⁴⁾). At NSSC, the characteristics of the slag are controlled by an index based on the composition, and the slag with good performance is selected.⁵⁾ The slag treatment methods at Nippon Steel and Nisshin Steel have not been reported.

To prevent the problem of fluorine leaching, development of refining processes that do not use CaF_2 , or the stabilisation of fluorine as a water insoluble compound with additives⁶⁻⁸⁾ can be considered. Although both technologies are under development, industrially effective measures are not established.

Principle to solve the dusting problem

Dusting is caused by the beta to gamma phase transformation of dicalcium silicate (C_2S) during cooling.^{9, 10)} This phase transformation can be suppressed if the slag basicity, *i.e.* the ratio of CaO to SiO_2 in the slag, is lower than in the dicalciumsilicate saturated region. However, the slag basicity must be high to promote desulfurisation during refining. Even though phosphorous oxide can stabilise the high-temperature crystal structure by forming a solid solution with C_2S , dephosphorisation during the refining process of stainless steel cannot be attempted as the severe oxidation of chromium occurs simultaneously.

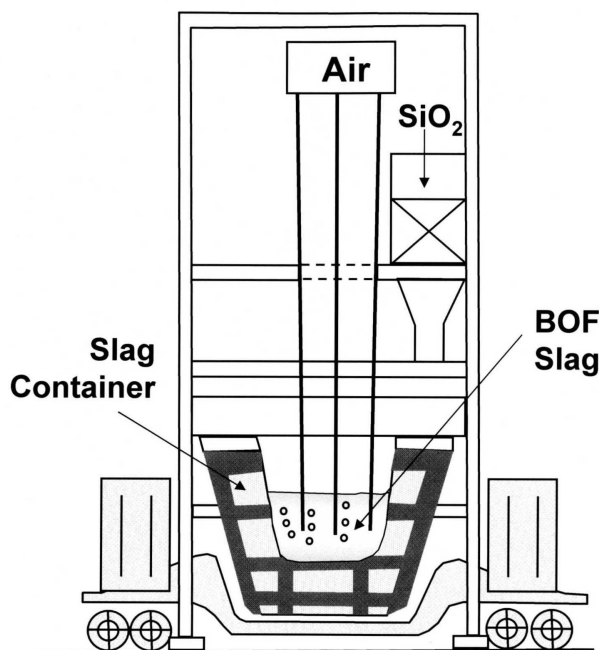


Figure 2: Slag modification process developed by Nippon Steel¹³⁾

For these reasons, to avoid dusting, a change in slag composition after refining is imperative. A method of adding borate to the slag has been established,¹¹⁾ which can also stabilise the high-temperature crystal structure. However, borate is rarely used due

to the leaching of boron from the slag to water.¹²⁾ The addition of silica sand or silica stone to the slag is another method. As a large amount of silica is necessary to decrease the slag basicity from the C₂S saturated region, a heating apparatus and a stirring unit must be installed to keep the slag in a liquid state and with a uniform composition. A slag modification process was developed by Nippon Steel in the late 1970s (Figure 2).¹³⁾ In this process, silica sand is injected to the slag bath with air to decrease the free CaO and free MgO content. Although this process would be applicable to stainless steel slag modification, this type of equipment is expensive.

Modification by mixing of nonferrous smelting slag

Preventing the dusting of stainless steel slag

Nonferrous smelting processes, *i.e.* the pyrometallurgical process of Cu, Pb, Zn *etc.*, emit slag that generally contains a high percentage of FeO and SiO₂. Nonferrous smelting slag with low basicity and high FeO can be considered as the optimum material for changing the composition of stainless steel slag. We have already proposed a slag modification process in which nonferrous smelting slag is mixed with stainless steel slag.¹⁴⁾

The fundamental experiments have been performed using the following methods. The industrial slag from the stainless steelmaking process and that of pyrometallurgical process of Pb–Zn smelting were mixed in an iron crucible. The compositions of the industrial slags are shown in Table 2. The crucible was placed inside a tube furnace for 1 h at 1658 K in an Ar atmosphere. After heating, the crucible was removed and cooled in an air atmosphere. The mixing ratio, defined as a ratio of nonferrous slag to the sum of nonferrous and stainless steel slag, was varied from 0.1 to 0.5. After the heat treatment, the modified slag was observed and recorded with a digital camera. The compositions of the modified slag were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Table 2: Average composition of the industrial slag

Process	Composition (mass%)							
	CaO	SiO ₂	T.Fe	MgO	Al ₂ O ₃	Cr ₂ O ₃	S	F
Stainless steel	50	29	1	13	2	1	0.2	4
Nonferrous smelting	12	22	35	4	8	0.5	3	0.2

The results are summarised in Figure 3 on the pseudo-ternary phase diagram of a CaO–SiO₂–FeO system, calculated by FactSage. When the mixing ratio became high, the dicalciumsilicate was no longer a stable phase, and dusting was prevented. In this experiment, the critical mixing ratio for forming lumpy slag was 0.2. Typical photos are shown in Figure 4. Also, as nonferrous slag is a uniform liquid, adding it increases the

modification rate of the stainless slag, compared to adding silica stone and iron ore.

For industrial applications, a calculation of the heat balance was carried out and the result is shown in Figure 5. In this calculation, nonferrous slag at various temperatures is assumed to be added to the tapped stainless steel slag of 1923 K. To keep the temperature above 1673 K, the maximum mixing ratio was about 15% when room temperature nonferrous slag is added. To add more nonferrous slag, changing the composition of nonferrous slag to a higher T.Fe and SiO_2 content, or installation of preheating equipment for the nonferrous slag is necessary.

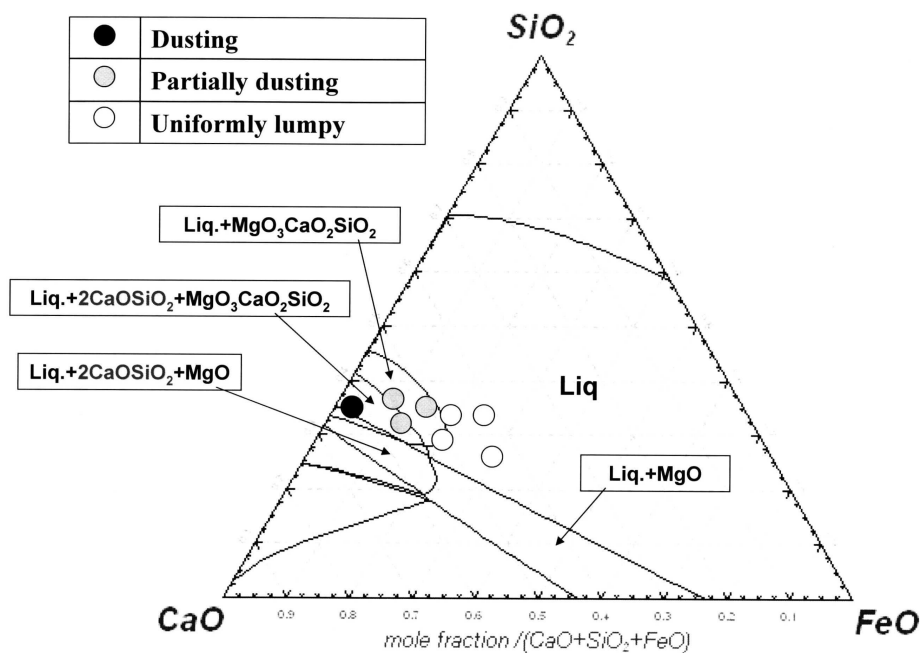


Figure 3: Dusting behaviour of stainless steel slag by the mixing with nonferrous smelting slag (the phase diagram was calculated at 1673 K, and the content of Al_2O_3 and MgO was 0.0265 and 0.11 in mole fraction, respectively)



Figure 4: Typical photographs of the slag after mixing treatment.

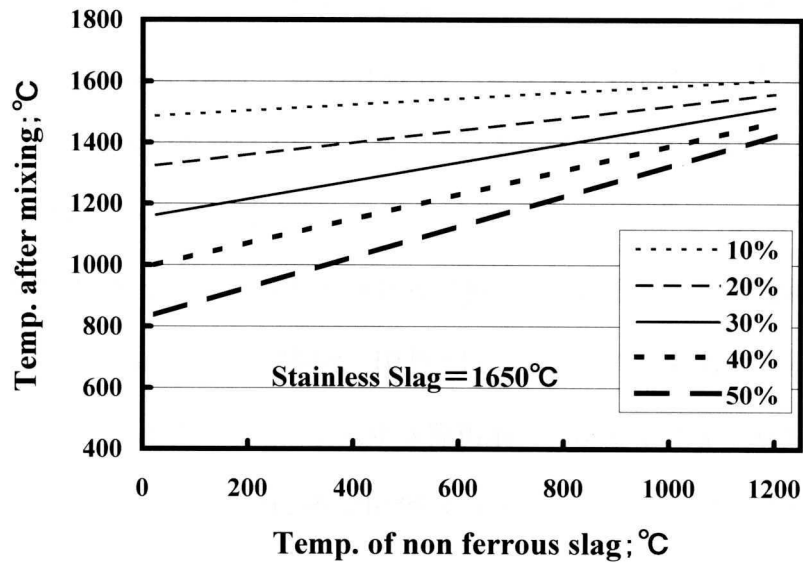


Figure 5: Simulation of slag temperature after mixing nonferrous smelting slag with the stainless steel slag

Behaviour of heavy metals in the modified slag

In some cases, nonferrous smelting slag contains heavy metals, such as Pb, Zn, Cu, *etc.* To utilise the nonferrous smelting slag as a modifier, the behaviour of the heavy metals has to be clarified. Compared with nonferrous smelting, the oxygen potential of the stainless steel slag is low, while the tap temperature is high. Therefore, the oxides of these heavy metals can be reduced by mixing with stainless steel slag. The concentration of heavy metal after mixing the stainless steel and nonferrous smelting slag was analysed. The results are summarised in Figure 6. In this figure, the analysed values are normalised by the calculated contents of each element, based on the mixing ratio, using equation (1).

$$C_{normalised} = C_{analysed} / (C_{nonferrous} \times R + C_{stainless} \times (1-R)) \quad (1)$$

where $C_{normalised}$, $C_{analysed}$ are the normalised and analysed content, and $C_{nonferrous}$, $C_{stainless}$ are the content in nonferrous smelting and stainless steelmaking slag, respectively, while R is the mixing ratio. As the normalised contents are lower than 1, the heavy metal content is greatly decreased after the mixing treatment. This is because:

1. As the TFe content in stainless steel slag is much lower than that of nonferrous slag, the heavy metal oxide can be reduced. ZnO, PbO, and CuO are reduced to Zn, Pb, and Cu, and evaporate or become sediment.
2. As the change in sulfur content shows the same behaviour as that of Cu, emulsified matte phases can be considered to settle out by the holding at high temperature.

On the other hand, the fluorine content was almost the same as the calculated value. Although the mixed slag is still inadequate to use as soil, it could be used as a material for road construction, civil engineering near the sea water, *etc.*

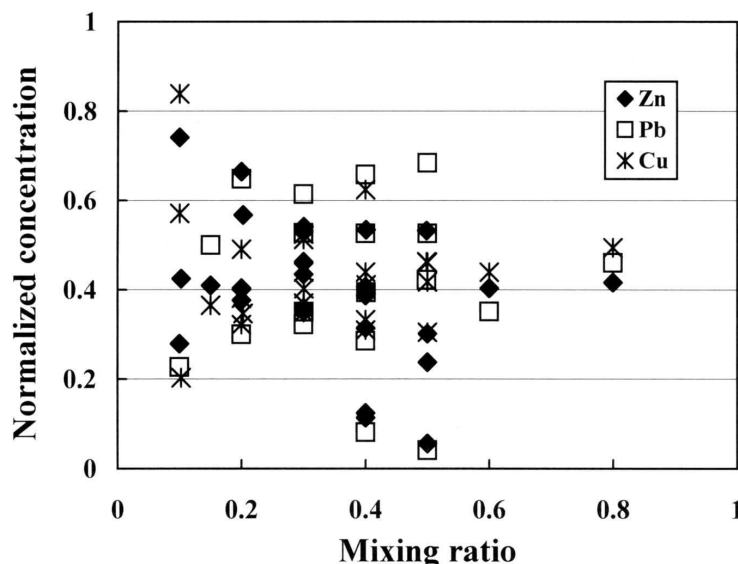


Figure 6: Behaviour of heavy metal concentrations by the mixing treatment

Conclusions

In Japan, stainless steelmaking technology can be divided into BF -BOF, SR-BOF, and EF processes. Depending on the process, slag of various compositions is generated. Although some slag treatment methods have been reported, the main problems for making the slag useful are dusting, volume expansion, and leaching of fluorine. From the reduction treatment after decarburisation with the addition of Si or Al, the problem of Cr^{6+} is not serious. To prevent dusting, we have proposed a new technology in which the nonferrous smelting slag is mixed with the stainless steel slag. Experiments showed that when the mixing ratio of nonferrous slag to total slag was higher than 0.2, dusting was prevented and lumpy slag was obtained. By the calculation of heat balance, to keep the temperature higher than 1673 K, the maximum mixing ratio was about 15% when room temperature nonferrous slag was added. The concentrations of heavy metals after mixing were much lower than the calculated values based on the mixing ratio.

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Chrome Immobilisation in EAF-Slags from High-alloy Steelmaking: Tests at FEhS-Institute and Development of an Operational Slag Treatment Process

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Abstract

Some EAF-slugs from stainless steelmaking can have insufficient properties to be used as construction material and may sometimes not meet the environmental requirements due to high leaching rates of chrome. FEhS-Building Materials Institute together with several European stainless steel producers has developed a method to increase the stability of these slags and to fix chrome in these slags. To meet the demands of a good construction material the liquid slag will be treated in order to stabilise the slag and to bind the remaining chrome in the slag into a stable slag phase. After having carried out several test runs in the FEhS-laboratory it seems to be possible to improve both the technical properties and the environmental behaviour of the slag by additions of materials which decrease the basicity and favour the formation of spinel type phases during solidification. To verify the successful results of the laboratory tests, industrial scale test runs at four melting shops of European stainless steel producers were executed. Also the results at the steel shops are sufficient. Thus it is possible to treat the EAF-slag from stainless steelmaking to produce volume stable and environmental friendly construction materials. So, even if the slag contains high chrome contents, the leaching of chrome will be suppressed.

Introduction

In stainless steel production, raw material costs dominate the total production cost for the primary product.¹⁾ Since chrome is one of the major constituents of stainless steel, it also represents a large portion of the raw material costs. Consequently, a high chrome recovery is essential for the overall process economy.²⁾ During melting of scrap in the Electric Arc Furnace (EAF), chrome is to a great extent oxidised into the slag. A reduction step is necessary both for the recovery of the chrome and to improve the environmental behaviour of the slag. Therefore, the reduction step in EAF stainless steel production has two important effects on its economy. Reduction of chrome from slags at stainless steelmaking is a presumption for further utilisation of the slag. Nevertheless, economically it is not possible to reduce chrome oxide from the slag completely. Therefore, it is necessary to bind the remaining chrome in stable mineral phases to suppress leaching. This target can be realised by modification of the liquid EAF-slag. Fluxes forming mineral phases of the spinel type are most suitable.

During the studies on the binding of chrome in the slag and the leaching behaviour of different EAF-slags from stainless steelmaking, the FEhS-institute has, together with some European partners, developed a slag treatment process by adding fluxes to the liquid slag during tapping, which induces the formation of chrome containing spinel-type phases in the slag during solidification.³⁻⁴⁾

Despite of the mechanical properties, the environmental compatibility is most important for the use of slags from stainless steelmaking. The latter will be expressed by their leaching behaviour in water.

To compare treated with non-treated slags, samples have been investigated on their chemical and mineralogical composition, their mechanical properties and their environmental behaviour. Other important influences on the environmental behaviour of slag are the melting history in the furnace, the melt temperature, the oxygen partial pressure during melting and of course the kind of materials used as slag formers, *e.g.* lime, limestone or dolomite etc. By evaluating these data, the first hints on the relationship between leaching and the contents of some oxides in the EAF-slags have been observed. This relationship has been the basis to develop the treatment process.

Laboratory investigations

Before starting with operational tests in the steel shop, laboratory tests have been carried out at the FEhS-institute to discover if there is any relation of, firstly, the slag composition or, secondly, the reduction with respect to the chrome binding. Several potential influencing factors were determined for different slag compositions as well as for the reduction of slag with coal, either by injection or in graphite crucibles.

As a result, no influence of the basicity of EAF-slags has been found. The observed effects by sand addition, which has been successful for BOF steelmaking slags,⁵⁾ could not be ascertained for these kind of slags. Therefore, further investigations on the reduction of slag have been carried out. At first, coal has been chosen as reduction agent. Coal is widely used in EAF steelmaking practise as reductant and slag foaming material. Due to the reaction:



chrome oxide is reduced to metallic chrome and CO. Due to thermodynamic equilibrium conditions not all of the chrome in the slag will be reduced during the laboratory tests. Thus the remaining chrome content in the slags after laboratory reduction is less than 1 wt% (without considering the reduced chrome in droplets, which are separated before analysing the slag). However, the reduced chrome is found in small

metal droplets in the slag, which will not segregate to form a regulus, due to the viscosity of the slag. The number of these droplets increase during the reduction time and their size grows. The chrome content in these metal droplets is up to 70 wt%. Spherical pores are found in the slag after carbon reduction and solidifying, which indicates that parts of the reaction gas is trapped in the slag and CO-precipitation occurs during solidification of the slag forming pores. Consequently, using carbon to reduce the chrome oxidation in laboratory tests will result in a porous solid slag.

Investigations on the leaching behaviour of the reduced slag show that the reduction of chrome content in the EAF-slag is no guarantee for low chrome content in the leachate. Even having achieved chrome contents in EAF-slags of less than 1 wt%, the leachability of chrome did not meet the environmental requirements in Germany.

It has to be stressed that these tests have been carried out aiming at slag reduction in the EAF stainless steel performance. Nevertheless, these tests have been also the basis for research activities on slag reduction and the reduction of other residuals containing chrome in specialised processes.⁶⁻⁷⁾

Laboratory tests to bind the remaining chrome

Evaluating slags generated in different stainless steelmaking plants, which use different process performances, different slag reduction practices and different slag formers, it has been shown that some of these parameters will have consequences on the leaching

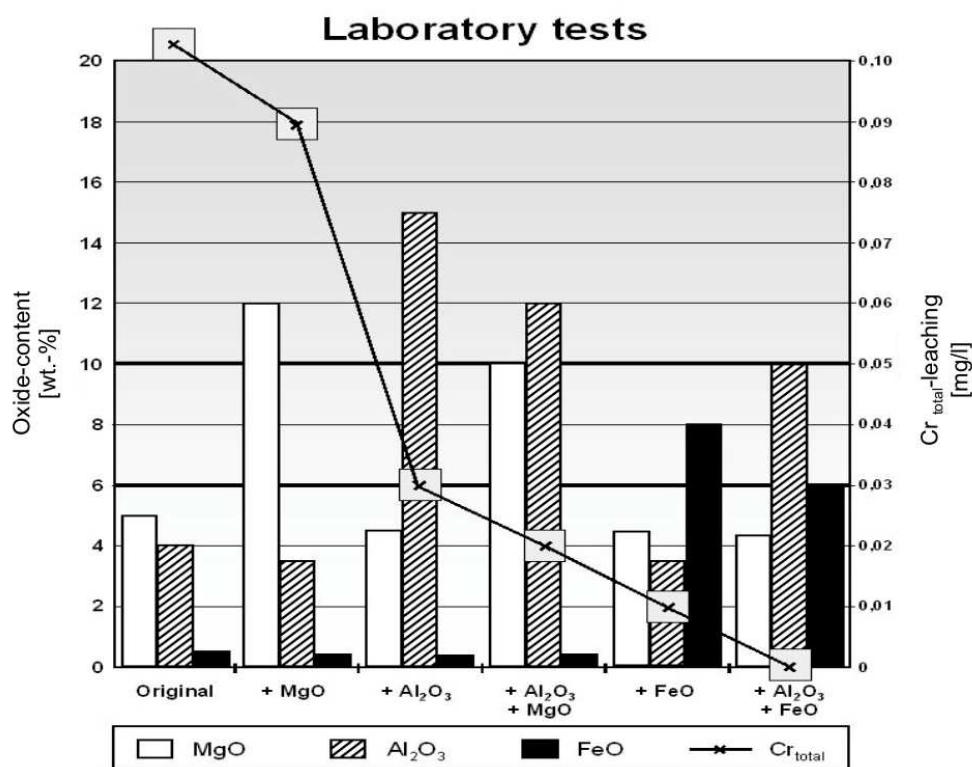


Figure 1: Results of laboratory tests on adding MgO, Al₂O₃ and FeO to liquid slags on the leaching of chrome

behaviour of slag.

Therefore, further research was aimed on fixing the remaining chrome content in the EAF-slugs into stable mineral phases. The results of the following laboratory investigations to fix the chrome into stable slag phases have shown a relationship between the MgO-, Al₂O₃-, FeO_n- and Cr₂O₃-content in the EAF-slugs from stainless steelmaking and their leaching behaviour of chrome (Figure 1).

Systematic investigations on the slag's mineral composition resulted in an increase of spinels in the slag matrix by additions of spinel forming materials, like MgO, Al₂O₃ and FeO_n, to the liquid slag. Chrome is bound by these spinel phases, which are stable compounds in the slag, Figure 2. The formation of spinel types Me^IO*Me^{II}O₃ (where Me^I is Mg²⁺, Fe²⁺ and Me^{II} is Fe³⁺, Al³⁺, Cr³⁺) will result in a strong binding of chrome and the Cr-leaching will be decreased to a very low level. Thus, the research work was concentrated on finding additions, which will induce the formation of spinel type phases during the solidification process of the slag.

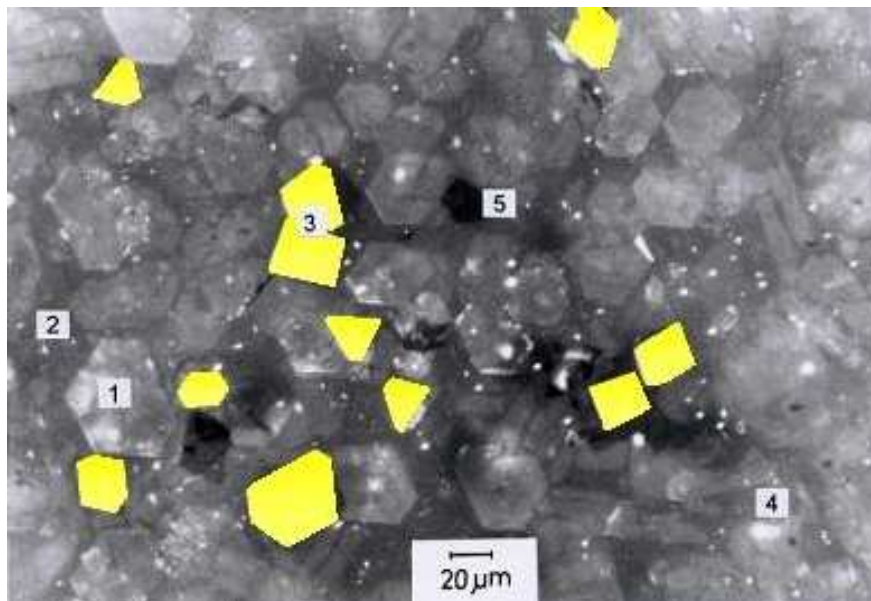


Figure 2: Mineral phases of an EAF-slag after treatment with Al₂O₃ (cubic spinel phases number 3 are marked)

Especially with regard to EAF-slugs from stainless steelmaking a proportional factor has been introduced to describe the influence of the different compounds in the slag on the binding efficiency of chrome into stable slag phases and on the leaching behaviour of chrome, respectively. The so called “*factor sp*” summarises the influence of the most important spinel forming compounds in the reduced EAF-slugs:

$$factor\ sp = a * MgO + b * Al_2O_3 + c * FeO_n - x * Cr_2O_3 \text{ [wt\%]} \quad (2)$$

Figure 3 shows the dependence on the leachability of chrome from reduced EAF-slags from stainless steelmaking concerning the “factor sp”. So, using this factor it is

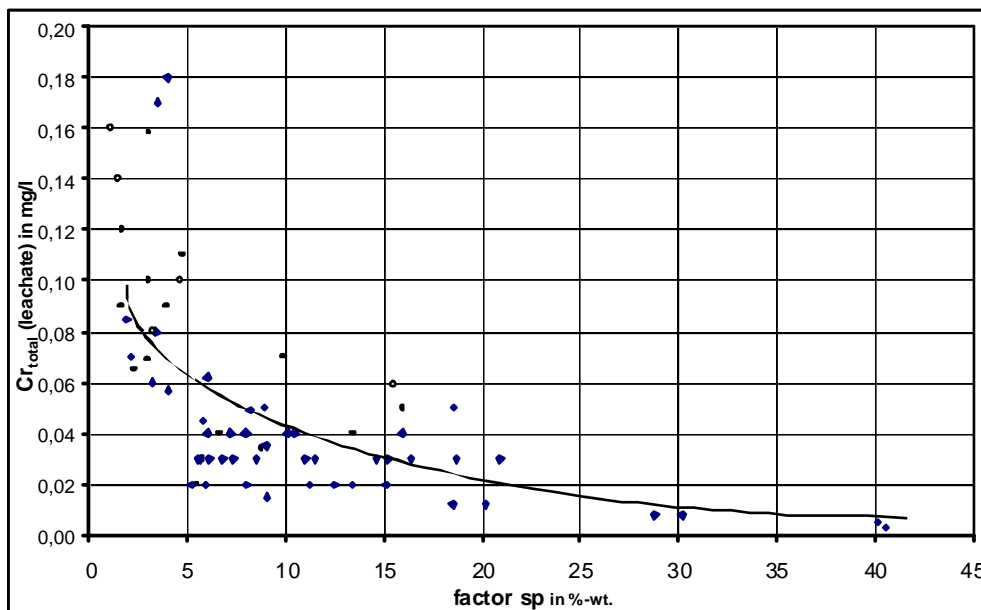


Figure 3: Chrome leaching of reduced EAF-slags from high alloy steelmaking versus “factor sp”

possible to evaluate the leaching behaviour of a slag from stainless steelmaking by knowing its composition. On the other hand, it is possible to evaluate the effects of adding spinel forming agents to the liquid slag on the leaching of chrome.

Operational tests

Having gained this knowledge on the influence of additions to the liquid slag on the binding of chrome by laboratory tests at the FEhS-institute, trials in steel shops of several stainless steel producers have been carried out to verify these laboratory results. In the following, three examples of successful treatment of liquid EAF-slag will be described.

Treatment of EAF-slag with bauxite

First, bauxite was chosen as addition, since this material contains both iron oxide and Al_2O_3 , which both have a strong influence on the leaching of chrome. Due to the usual composition of EAF-slags, the quantity of bauxite-addition has been calculated, aiming at a slag composition with an Al_2O_3 -content higher than 10 wt%. Such a slag will achieve a sufficient “factor sp”. Bauxite (< 5 mm) has been added in portions of approximately 600 kg into the transfer ladle during the slag and steel tapping from the

EAF to get an intensive mixing between slag, steel and addition, as a basis for the expected chemical reactions.

Slag samples from the slag yard have shown that due to the homogeneous distribution of Al_2O_3 and FeO_n in the slag the dissolution of bauxite was complete. Due to the resulting contents of Al_2O_3 and FeO_n the “*factor sp*” was increased to more than 15 wt%. Consequently, the examination of the leaching behaviour of the slag according to the German leaching standard DIN 38414-4 S4 has shown that the leaching of chrome is decreased to the detection limit. Thus, these first in-plant tests confirm the relationship expressed by the developed “*factor sp*”. Furthermore, this first treatment of liquid slag in the transfer ladle by addition of bauxite has exhibited the feasibility to optimise EAF-slags from high alloy steelmaking with respect to their environmental behaviour. The aim to bind the remaining chrome in the slag into stable spinel phases has been reached.

But some new experiences have been gained concerning the use of additions in practice. The time of adding the treatment agent is important. The most suitable time is when the transfer ladle is filled to one third. This guaranties a good mixing in the ladle. Also very important is the grain size of the material to be added. Best results will be achieved by adding materials with a grain size of *e.g.* 3-8 mm. The test results allowed to plan additional tests at a pilot scale level at other steel shops of stainless steel producers. Since the addition of bauxite to a low value product seems to be too expensive, other suitable materials have to be used. Due to the experiences in laboratory and good results from the first operational tests, residues with a high alumina content have been chosen for further tests.

Treatment of EAF-slags with Al_2O_3 -containing residues

Different mixtures of oxide materials have been investigated, and finally a material called TE 75 (75-85 wt% Al_2O_3 and 10-20 wt% SiO_2) was selected, which seems to be suitable for the treatment of EAF-slag. The grain size of TE 75 was 3-8 mm. This material has been tested at the EAF of one of the stainless steel producers. An installation to add alloying agents to the steel during tapping was revised, in order to use it for the addition of spinel forming agents into the slag during tapping. The first transfer ladle was filled up nearly “slag-free”, and during tapping steel and slag into the second transfer ladle the spinel forming agent was added, Figure 4. The small amount of untreated slag in the first transfer ladle was sampled as reference. Additionally, the treated slag in the second transfer ladle and in the slag pot was sampled to determine the effects of the addition. The amount of the addition was calculated according to the “*factor sp*” and the actual EAF-slag composition.

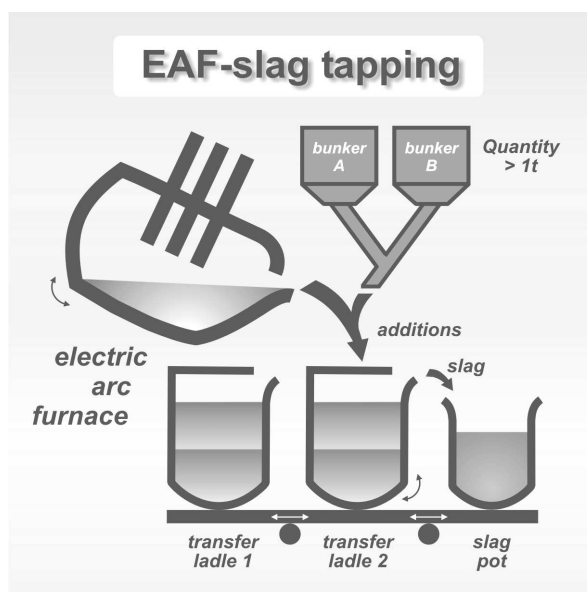


Figure 4: Tapping practice of steel and slag at one EAF

According to the treatment the Al_2O_3 -content and thus the “*factor sp*” are increased in the slag (Figure 5). Due to the added SiO_2 in the mixture, the basicity CaO/SiO_2 in the slag is decreased to about 1, which corresponds with better technological properties, as shown later. The most important effect, however, is the leaching of chrome. In accordance with the earlier investigations a high “*factor sp*” results in low chrome leaching.

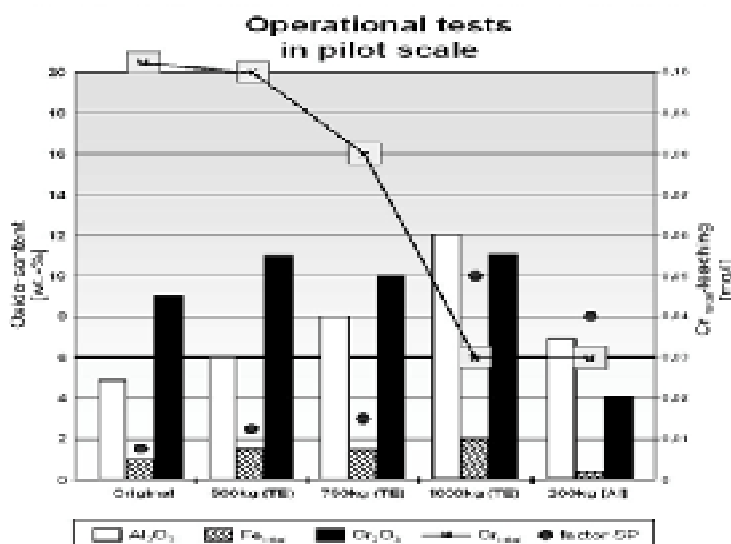


Figure 5: Results of one pilot operational test campaign at one steel works: relationship between different compounds in the slag, “*factor sp*” and the chrome leaching

At the end of five test campaigns to treat EAF-slags at one steel shop with the oxide mixture TE (Al_2O_3 -containing material) 10.000 tons of optimised EAF-slags with sufficiently sound environmental and technological properties were produced.

Reduction of EAF-slags and increasing “*factor sp*” with aluminium

In a third step the Al_2O_3 -content of the EAF-slags was increased by reducing the slag during tapping with metallic aluminium. The aim was first of all to recover the chrome into the steel, but secondly to increase the alumina content in the slag. So, two effects have been achieved: firstly by increasing the “*factor sp*”, which has a positive consequence on the chrome leaching, and, secondly, the reduction of the Cr_2O_3 -content to recover Cr into the steel combined with an increase of Al_2O_3 in the slag, resulting from the oxidation of the added aluminium.

The operational campaigns have shown the expected positive effects on the environmental behaviour of the treated EAF-slags. The reduction with aluminium results in higher Al_2O_3 - and lower Fe_{total} - and Cr_2O_3 -contents in the treated EAF-slags. By a suitable quantity of aluminium and correct timing of the addition during tapping of steel and slag into the second transfer ladle, the chrome content in the leachate is less than 0,03 mg/l (Figure 5) and is so in the range of the characteristic value given for EAF-slags from carbon steelmaking in Germany.

Finally, 4.000 tons of optimised EAF-slags were produced during these campaigns using aluminium to reduce the EAF-slags. These slags have shown overall good environmental behaviour and good mechanical properties, too.

Technical properties of the operational treated slags

In general all the treated slags were volume stable. A disintegration due to the dicalciumsilicate transformation (α - to γ - C_2S) does not have to be taken into account, since the treated slags have basicities CaO/SiO_2 less than 1,5. The free lime content in treated EAF-slags is negligible, so that no volume increase due to $\text{Ca}(\text{OH})_2$ can occur.

The strength of the treated EAF-slag from stainless steelmaking is similar to that of EAF-slag from carbon steelmaking. In Figure 6 the mechanical properties of the EAF-slag concerning strength and abrasion are given. A low value (as determined by performing the impact test) characterises a slag with high strength. A high PSV-value characterises a high abrasion resistance. Additionally the slag shows high “SCRIM-values” which stand for a good grip of tyres especially of asphalt surfaces layer.

In summary, it can be said that the results of the research work have shown that treated EAF-slag from high-alloy steelmaking should be considered as a highly valuable material.

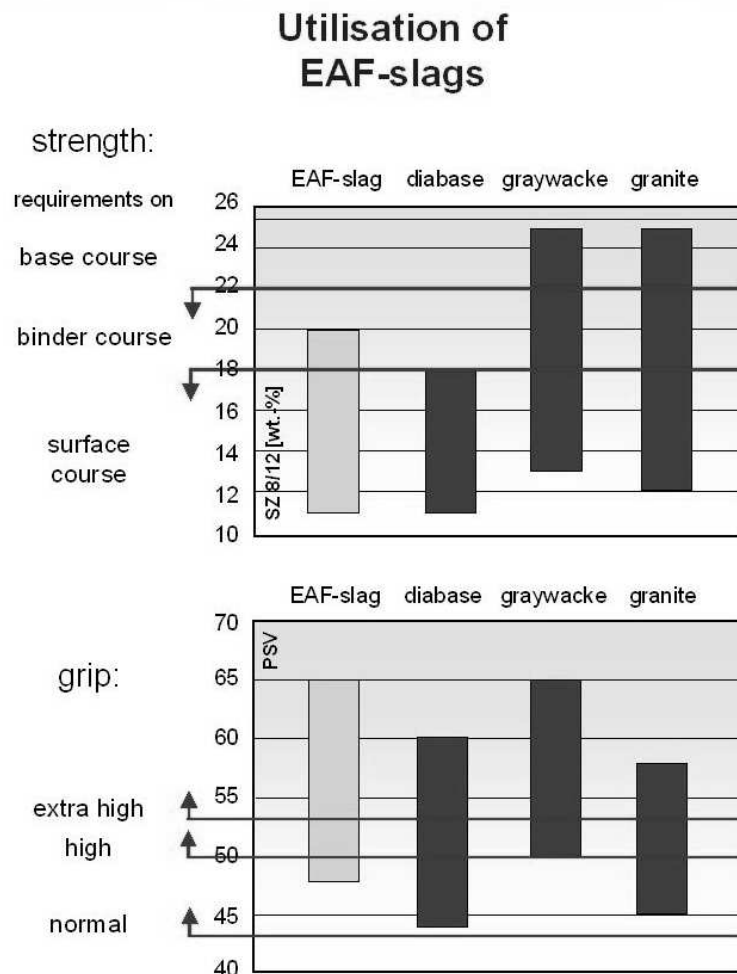


Figure 6: Some results of testing the mechanical properties of treated slag compared to some natural aggregates

Conclusions

The aim to fix chrome in EAF-slags from high-alloy steelmaking into stable spinel phases has been achieved. The mechanical properties of the treated EAF-slags are satisfactory for fields of application with highest quality demands.

A new method of treating EAF-slag from stainless steelmaking has been developed. During tapping of the steel and slag, agents are added into the liquid slag, that induce the multiple formation of spinel type phases in the solidifying slag. The effects of

different spinel forming additions to reduced EAF-slugs can be described in a formula developed as result of the investigations:

$$factor\ sp = a * MgO + b * Al_2O_3 + c * FeO_n - x * Cr_2O_3 \quad [wt\%] \quad (3)$$

For slugs with low values of “*factor sp*” the leaching of chrome is high. For EAF-slugs showing high values of “*factor sp*” chrome leaching is nearly negligible. As a consequence this formula developed by FEhS-institute is used by some works to characterise their slugs, today.

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Session 3

Slag valorisation and regulation

REACH, Registration of Iron and Steel Slags – State of the Art

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Abstract

The REACH regulations are in force since 1st June, 2007, which will have consequences for the iron and steel industry. In this paper it is shown that the FEhS-Institute and EUROSLAG have developed a procedure that will allow for the successful registration of iron and steel slags within REACH. It is highlighted that the REACH registration actually reinforces the long standing opinion of the steel industry in Europe to produce and sell iron and steel slags as *products*.

Introduction

The new European regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) was adopted by the European Parliament and the European Council in December 2006 and came into force on 1st June, 2007.¹⁾ The regulation comprises the following substances:

1. Phase-in-substances subject to admission control:
2. Phase-in-substances subject to registration:
3. New substances.

“Phase-in-substances” are substances which have been put on the market before 18th September 1981. This is why “new substances” are all substances which are put on the market after this date. 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).

For phase-in-substances registered in EINECS a transition period is admitted for the final registration in REACH. To be able to use this transition period, it has been essential to pre-register the phase-in-substances, if more than 1 ton/year was produced before 1st December 2008. If a substance has not been pre-registered, it is not possible to occupy the transition period ending 1st December 2010 for phase-in-substances according to article 23 (special conditions for phase-in-substances). Such substances have to be treated like new substances and have to be registered after the pre-registration period, directly. Otherwise, such substances (without registration) must not be put on the market. Although the pre-registration is not obligatory, a pre-registration

for all substances that come into consideration has been recommended, since this registration is exempted from charges and does not result in a registration, necessarily. The process of registration can be cancelled after pre-registration, if necessary.

The procedure developed by FEhS/EUROSLAG

Just after implementation of the REACH regulation, the members of the FEhS-Institute and EUROSLAG have decided to register iron and steel slags as substances. Due to expertises and agreements with environmental authorities these substances are established as by-products in Belgium, Finland, Germany, Austria and the United Kingdom. In this context it is relevant to refer to the decision of the European Commission from 21st February 2007 to accept blast furnace slag as by-product.²⁾ On the other hand, iron and steel slags are registered as phase-in-substances with corresponding EINECS and CAS numbers. Provided that slags are no wastes but products, the *ad hoc* working groups “REACH” of the FEhS-Institute and EUROSLAG have started the pre-registration work on iron and steel slags aiming at the final registration before 1st December 2010. Fundamental for their further work, slag families have been described as shown in Table 1, compiled on the basis of the existing CAS and EINECS numbers.

Table 1: Grouping blast furnace and steel slags

Slag Family	Material	CAS no	EINECS no.
GBS	Slag, blast furnace (granulated)	65996-69-2	266-002-0
ABS	Slag, blast furnace (air cooled)	65996-69-2	266-002-0
BOS	Slag, converter	91722-09-7	294-409-3
EAF C	Slag, electric arc furnace (carbon steel production)	91722-10-0	294-410-9
EAF S	Slag, electric arc furnace (high alloy steel production)	91722-10-0	294-410-9
SMS	Slag, steelmaking	65996-71-6	266-004-1

The members of the FEhS-Institute and EUROSLAG have pre-registered these slag families before 1st December 2008, uniformly. Data sheets have been drafted. Table 2 gives – as an example – the data sheet for air-cooled blast furnace slag. In addition to the information on the composition and generation of the slags, these data sheets contain also information on the applications, which have to be observed according to the final registration. They have been summarised as follows:

- Constituent for the production of hydraulic binders;
- Addition to concrete;
- Building material;
- Fertiliser;
- Sand blasting material;
- Component for the production of glass.

For a long time it has been discussed, especially with the European steel producers incorporated in EUROSILAG, how iron and steel slags have to be classified in accordance to the document “Guidance for identification and naming of substances under REACH”³⁾. According to the decision tree described in this document, the slags possibly can be grouped into “mono-constituent substances”, “multi-constituent substances” or as “UVCB-substances” (Substances of Unknown and Variable composition, Complex reaction products or Biological materials). The discussion within the members of the FEhS-Institute resulted in the view that apart from secondary metallurgical slags, blast furnace and steel slags should be classified as “multi-constituent substances” as the variation of the chemical composition of these slags and their mineralogical phases are well-known since a long time.

However, the European Chemicals Agency (ECHA) has finally decided that, according to their developed registration tools, only the groups “mono-constituent/UVCB” or “multi-constituent” with known CAS and EINECS numbers have to be used. In general, for iron and steel slags, the group “mono-constituent/UVCB” was foreseen. However, the reasons for this decision are unknown. It is assumed that the decision was made against the background of the mentioned guidance document that generally groups slags as UVCB-substances without knowledge of generation and source. So the question how to group slag will be discussed again during the final registration of iron and steel slags.

Within the framework of pre-registration additional numbers had to be given concerning the amount of annual production of slags. Since the amount of yearly production for iron and steel slags is always above 1000 ton/year, a registration before 1st December 2010 is necessary.

For the pre-registration and later on also for the registration the producers of slags have to register their own products. That is why the European steel plants pre-registered the relevant slag families with regard to Table 1. There was a strong discussion about the question how to proceed with regard to pre-registration and finally to registration if a cement producer is owner of a slag granulation unit. In such a case the cement producer is a producer of granulated blast furnace slag too. The same situation may apply to plants processing blast furnace or steel slags taken from old heaps.

That situation has been discussed within the REACH working groups controversially, too. Finally the decision has been made that with regard to cement plants the producer of the hot metal (steel plant) will register the slag product, since the chemical composition of the slag will be specified in the blast furnace and will not be changed during granulation. But according to the processing of old slag heaps the owner of the processing plant has to be regarded as producer of the slag and will be responsible for pre-registration and, finally, registration.

Table 2: Pre-registration data sheet for air-cooled blast furnace slag

Slag, blast furnace [air cooled]	
EINECS no.:	266-002-0
CAS no.:	65996-69-2
Other identity code:	BF slag is defined in EN 14227-2:2004-07 "Hydraulically bound mixtures - Specifications - Part 2: Slag bound mixtures". This standard has been developed by CEN/TC 227.
Substance identity: multi-constituent substance (for input IUCLID 5: mono-constituent/UVCB)	
Name and address of the producer/importer: ...	
Name of the responsible contact person and his/her substitute: ...	
Blast Furnace slag is a by-product of the manufacture of iron by chemical reduction in a blast furnace. It is formed in a continuous process by the fusion of limestone (and/or dolomite) and other fluxes with the residues from the carbon source (coke) and non-metallic components of the iron ore. Blast Furnace slag is produced at temperatures around 1500°C. Dependent on the way of cooling it can be distinguished between crystalline air-cooled blast furnace slag and glassy granulated blast furnace slag.	
Quantity produced during one year:	> 1000 t
Fields of application (industrial/professional):	constituent for hydraulic binders, construction materials, fertilizer, raw material for glass-making
Major Mineral Constituents	Molecular and structural formula
Melilite (solid solution between akermanite and gehlenite), calcium-aluminium-magnesium-silicate	$\text{Ca}_2\text{MgSi}_2\text{O}_7\text{-Ca}_2\text{Al}_2\text{SiO}_7$
Merwinite, calcium-magnesium-silicate	$\text{Ca}_3\text{MgSi}_2\text{O}_8$
Pseudowollastonite, calcium-silicate	CaSiO_3

Today, all European steel works have finished the pre-registration of their slag products. ECHA has already published a list of the pre-registered substances and now has to allocate the different materials to Substance Information Exchange Fora (SIEFs). It is not yet clear how the iron and steel slags will be grouped. There will be established so called pre-SIEFs, so that the producers of the substances have the possibility to check, in which SIEF their substances will finally be grouped in.

After having completed the pre-registration, the final registration has to be started as soon as possible. For this purpose the FEhS-Institute intends to form a consortium "iron

and steel slags”, open to all European producers of iron and steel slags. The necessary activities to prepare a consortium agreement are nearly finished, so that a first general assembly will be convened on 20th May 2009 at Düsseldorf. Nevertheless, the members of FEhS-Institute have launched a cluster under a pre-agreement respecting especially the co-operation under anti-trust law conditions. This cluster already works since May 2008 to prepare the registration dossier. The FEhS-Institute decided to work together with a consultant coming from the chemical industry, to prepare an overview on the lack of data necessary for registration and to start with closing the gaps with new investigations, especially on the human and ecotoxicity of blast furnace and steel slags.

All results, that are compiled within the frame of the cluster, will finally be available in the European consortium “iron and steel slags”. The tasks of the consortium are to work out the registration dossiers. Based on the software tool IUCLID 5 the necessary dataset for drafting the safety evaluation report (Chemical Safety Assessment “CSA”) will be finalised. The final registration dossier has to be sent to ECHA before the end of May 2010 by the lead registrant. In general, the registration of iron and steel slag will be carried out as “joint registration”. So meanwhile some members of FEhS-Institute have been elected, to deliver the registration dossiers as lead registrant for the relevant slag families before the end of May 2010 at the latest to ECHA, see Table 3. The other members of the consortium may use this information for writing their own registration dossiers.

Table 3: Lead registrants for blast furnace and steel slags

Slag Family	Lead Registrant
GBS/ABS	ThyssenKrupp Steel AG, Duisburg
BOS	ThyssenKrupp Steel AG, Duisburg
EAF C	Stahlwerke GmbH, Kehl
EAF S	ThyssenKrupp Nirosta GmbH, Duisburg
SMS	ThyssenKrupp Steel AG, Duisburg

Conclusion

By the procedure shown above, the members of the FEhS-Institute and EUROSILAG are assured, that the registration of iron and steel slags within REACH will be achieved successfully. At the end, the registration reinforces the long standing opinion of the steel industry in Europe, to produce and sell iron and steel slags as products.

References

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Legal Status of Slag Valorisation

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Abstract

Slag used as aggregate in different kinds of utilisations can be divided into 2 groups: Blast Furnace Slag and Steelmaking Slag. Legislation for using aggregates differs in every country, but changing laws in Europe and outside ask for new and inventive ideas for use as well as to provide opportunities. Slags will probably become a by-product, but have to take into account any possible adverse environmental effects of the substance or object. End-of-waste criteria are to be defined yet, which is not easy because every country has its own leaching method to determine the risks. Harmonisation of tests will make this easier. To valorise slag, however, research, cooperation with and education of civil servants, engineers and the public is necessary.

Introduction

Looking at the title of this article one could think: is valorisation of slag aggregates bound to legal environmental principles? After all, slag is similar to natural aggregates and these aggregates are exempted from REACH and do have value, because they are essential in our society. Of course value comes with demand: no demand, no value. But sometimes demand is coming from creative minds, sometimes it is a change in the political agenda, sometimes it is pure necessity. Whatever the reason may be, using slag with whatever value is bound to certain laws. Restrictive or supportive, the EU legislation is intended to improve trade and competitiveness as well as to protect the environment and human health at the same time. It is there where the valorisation of slag gets into a tight corner. To add value to slag and its use, investments, research, education and advertising with positive examples are necessary. Although the present economical situation is not very favourable for by-products, residues and wastes, materials such as slag keep their value as a raw material substitute both internally in the steel company and on the market. However, to compete with natural aggregates and to fulfil all legislative requirements, there is an inevitable need for quality improvement, new uses, quality control and process control.

Slag has a long history in use as valuable road and building material. During the Iron Age, slag was used as pavement for roads. Many Roman roads were made and reinforced with slag. From the Celtic period it is known that slag was used for walls around villages, as for example in Germany. Also known from Germany are the Slag

Cannon balls made of Iron Slag.¹⁾ Furthermore, slag stones were used for masonry and were applied in pavements as well.

In modern times, slags still have a value. How high this value is, depends on the type of utilisation. A major difference with the old days is that usage of slag is bound to stringent rules, which, furthermore, differ all over the world. In Europe, slag is mainly bound to the Waste Framework Directive (WFD). Slag as a product has to comply with the REACH regulations in the near future. Concurrently, using slag as secondary building material has to comply with other legislation. Slag that cannot be used has to be landfilled. This slag has to fulfil the Landfill directive. Laws like these are known in the USA, Asia and Oceania as well. This article will mainly focus on the European situation, but comparisons will be drawn with other countries if applicable. Examples of new and valuable utilisation types will be given and checked with legislation.

Utilisation of Slag

Within the Iron and Steel industry slag can be divided into two groups: Blast furnace slag (BFS) and Steelmaking slag (SMS). Both slag types are preferably used in different ways with high added value, but a certain overlap in use is inevitable.

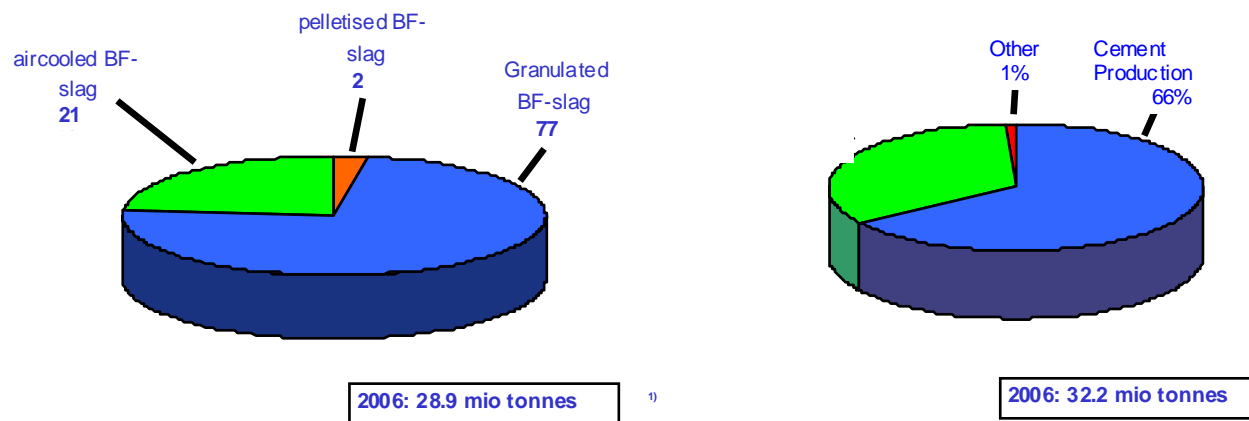
Blast Furnace Slag

In Figure 1 (graph 1), an idea is given of the amount of BFS produced in Europe and its utilisation. BFS is produced as Granulated Blast Furnace Slag (GBFS), Air Cooled Blast Furnace Slag (ABFS) and Pelletised Blast Furnace Slag. The GBFS is liquid slag that has been cooled down with a forceful water spray, granulating the BFS in glass like grains. ABFS is slag left to cool down to air forming a wide range of grain sizes.

The second graph of Figure 1 shows that more (G)BFS is used than produced. The reason for this difference is that old stocks are reworked. (G)BFS has a high product value as a replacement for clinker in cement and as a constituent of concrete. Throughout Europe there are, however, differences in what is allowed with GBFS. In Spain for instance, it is not allowed to use GBFS in concrete, but it is allowed in cement. In Germany it took many years of research and discussion to use it in cement and concrete. The former steel company Krupp used BFS for cement in the 1920s. In the Netherlands it was quickly accepted as a valuable additive in concrete and used for the so called Delta Works to protect the southwest part of the Netherlands from flooding. GBFS concrete is known for its seawater resistance. In IJmuiden, a special GBFS cement plant was erected close to the Blast Furnaces in 1930. Environmental benefits of Ground Granulated Blast Furnace Slag (GGBFS) as substitute for clinker include the reduction of CO₂ emissions to air and energy savings. GGBFS contains CaO and, therefore, less lime has to be burned or decarburised. Furthermore, it has a

relatively high reactivity. Depending on the type of concrete, the mixtures of GGBFS and clinker differ. Because of its high market value, GGBFS is transported from Japan to the USA. In 2006 40% of the GGBFS of Japan was shipped.³⁾ GGBFS is also shipped from Finland to Spain and from Holland to Ireland.

Air cooled Blast Furnace Slag is partly used for road construction and after having been crushed into sand size grains, it is used as part of special slag bound road mixtures. Remolten BFS together with certain minerals is used to make slag or mineral wool for insulation. This special procedure is done for instance in the UK and USA.



Data from: A, B, D, E, F, FL, I, NL, S, UK

Figure 1: Production and utilisation of Blast Furnace Slag throughout Europe in the year 2006²⁾

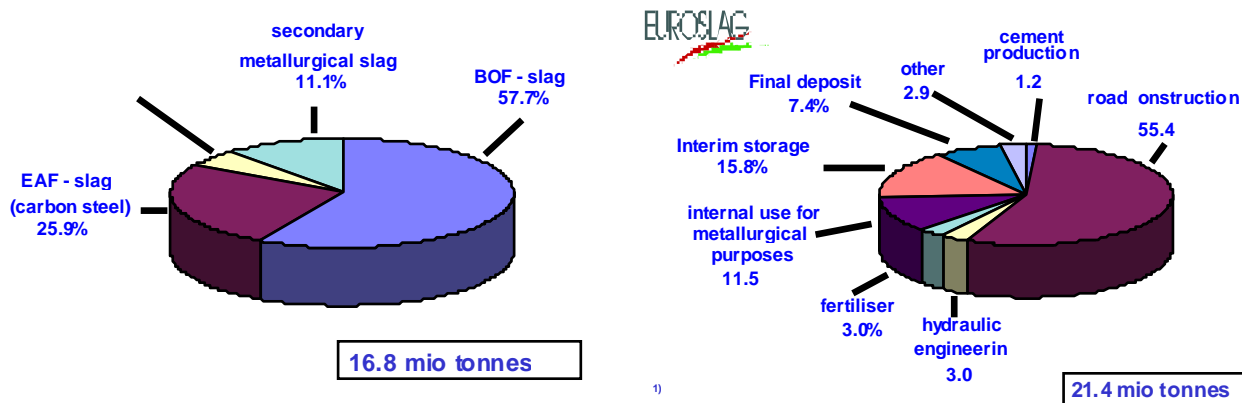
Steelmaking Slag

In Figure 2 the production of Steelmaking slag and its utilisation is depicted. Here the utilisation is also more than the production because old stocks are reworked. Within the steelmaking slag group, 3 subgroups can be distinguished: Converter slag, Electric Arc Furnace (EAF) slag from Carbon and Stainless steel and (Secondary) Steelmaking Slag.

BOF slag constitutes the majority of the steelmaking slag types. This type of slag is produced mainly in Western and Northern Europe. The iron source is hot metal from the blast furnace. The hot metal contains silicon, carbon, phosphorous and manganese as main components and metals as important residuals. These elements are transferred into the slag during the steelmaking process. To make slag, lime and dolomite are added. Therefore, this slag contains free lime, Ca-Mg-ferrites and dicalciumsilicates. The most valuable utilisation types are in asphalt, cement industry and as armour stone for dikes and dams. For certain uses, the slag is allowed to have only a low volume expansion

level, as is the case for asphalt and concrete. However, the expansion rate differs from country to country, for instance for asphalt 0-3 % in Holland and Germany, but up to 5% volume expansion in the UK.

Stabilising LD slag is a method to improve the slag for asphalt pavements and even in concrete. DSU in Germany has developed a method to stabilise the slag by blowing SiO_2 and Oxygen in liquid LD slag. In this way, the free lime binds to quartz to form dicalciumsilicates (Larnite). The oxygen is needed to generate heat. Fully operational installations are at Thyssen Krupp in Duisburg, Germany and at Sidmar in Ghent, Belgium. This so called Lidonite[®] has a high value on the market.



Data from: A, B, D, DK, E, F, FL, L, NL, PL, S, SLO, UK

Figure 2: Production and utilisation of Steelmaking Slag throughout Europe in the year 2006²⁾

In China, MultiServ has two sites where they process steel slag. In Hang Zhou the BOF slag is ground with a rod/ball mill into microns and used in concrete of high durability. Grinding processes are expensive in Europe, but in countries like China cheap enough to perform.

EAF slag is mainly produced in Southern Europe and parts of Northern Europe. Mainly scrap is used as iron provider in the process. To make slag, lime and dolomite or magnesite is used to capture all the impurities. Metals are added for alloying. The slag is less lime rich than the BOF slag and, therefore, very stable. Because of this stability it can be used in asphalt without any problems. Utilisation is more or less the same as is the case for BOF slag. From the added alloys a part is transferred to the slag.

In Europe and the USA research is done to use steel slag for rail tracks. In Germany Dr Th. Merkel from the FEhS Institute in Duisburg has performed such experiments.⁴⁾ Until now, only Air cooled BFS was allowed but the tests showed no problems and the German Railroad company accepted the material for railway foundations. The precondition is sufficient volume stability such as in EAF and low free lime BOF slag.

Secondary Steelmaking Slag is the most instable type of slag. Part of the slag tends to fall apart shortly after it is tipped in the pits. The γ -type dicalciumsilicate is responsible for the decomposition of this slag (*see other contributions in these Proceedings*). Therefore, a stabiliser like Borax has to be added. In Slovenia, extensive research has been done by Rozman *et al.*⁵⁾ showing that the high $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ slag was successfully stabilised with Borax, added during the process. In this way, the slag became usable and therefore valuable.

Ladle Slag from Secondary Steelmaking, cf. from vacuum treatment or stirring stations, can be used in the cement industry as an aluminium deliverer. At the moment trials are performed in Europe, where from different steel plants Ladle Slag is transported to a cement plant. In that plant the Ladle Slag is used instead of bottom ash.

Unfortunately, a part of the Steelmaking slag is still landfilled. This is partly because of the high production volume, market demand, slag quality, reputation, and local legislation. In Italy, for instance, it is hard to use any slag as road foundation or otherwise. In Spain the culture is to use other aggregates. Bureaucracy in Spain is a barrier to sell slag as well. Furthermore, natural aggregates are still very cheap. Contractors own their own quarries and are therefore able to produce cheap and transport aggregates in large vessels all over the world.

Legislation

The main laws and legislations concerning the use of slag are European laws or protocols the EU and its individual Member States have signed and put into action. However Member states interpret directives and legislation in very different ways. The following legislation will be discussed hereafter:

- The Kyoto protocol;
- The Reference Document of Best Available Techniques;
- The Waste Framework Directive;
- Harmonisation Committees TC 351 Dangerous Substances and TC 154 Aggregates;
- The REACH directive (*which is discussed in these Proceedings by Dr. H. Motz*).

The Kyoto Protocol

The Kyoto Protocol on CO₂ reduction was drawn in 1997 and has been fully operational and in force since 2005. This Protocol tries to regulate and decrease CO₂ emissions down to the 1990 CO₂ emission levels. After 1997, many conferences on the implementation of the Protocol have been held. In 2005, the Intergovernmental Panel on Climate Change (IPCC) wrote a report on Carbon Dioxide Capture and Storage.⁶⁾ In 2007, the Fourth Assessment Report (AR4) on Global Warming was published by the same IPCC.⁷⁾ These reports confirmed the ideas about global warming, the role of CO₂ and other greenhouse gasses, but the reports also described ways to sequestrate CO₂ and diminish the CO₂ contribution to warming the earth.

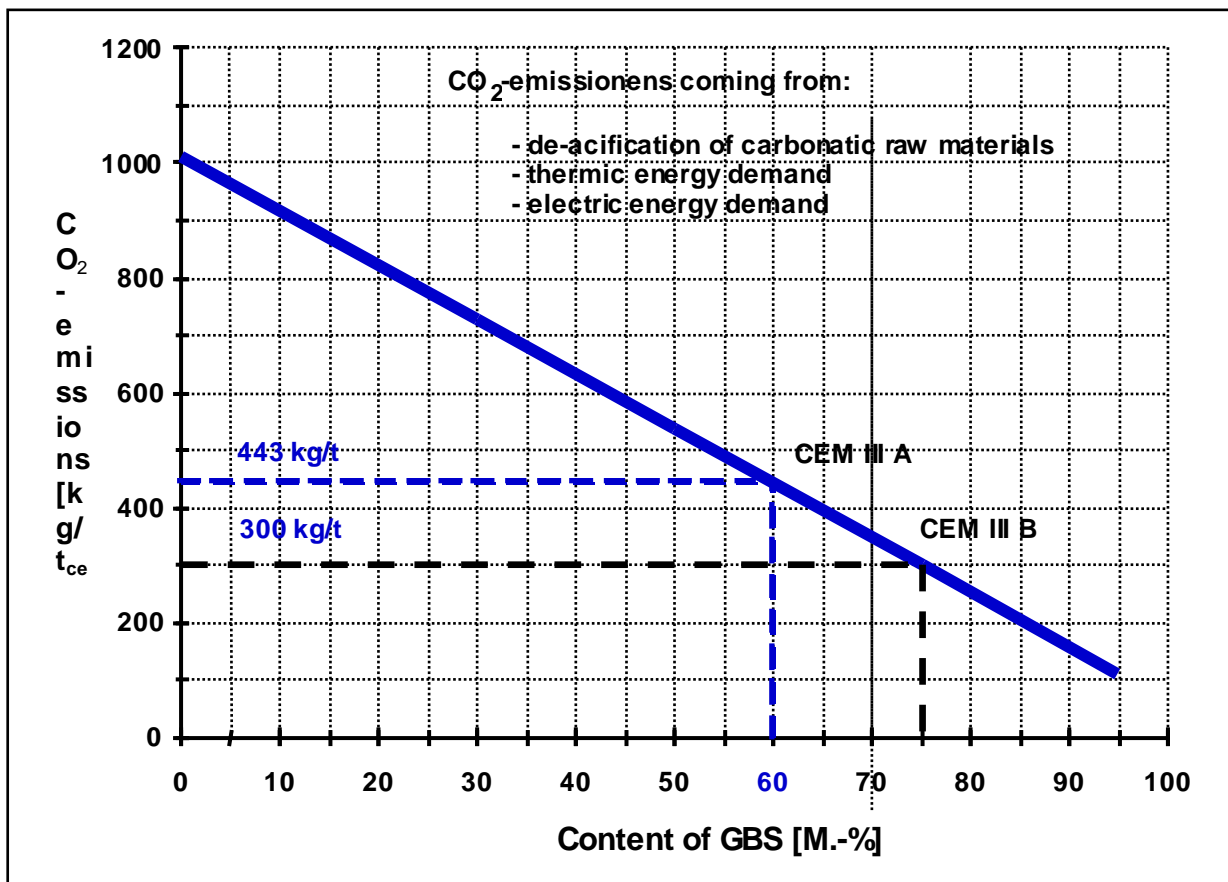


Figure 3: Relation between CO₂ emissions and utilisation of GGBFS²⁾

Due to these developments the EU promised that they would reduce CO₂ emissions with 20% in regard to the CO₂ emission levels of 1990. The Netherlands even went as far as 30% reduction with respect to the 1990 level. To accomplish these ambitious reductions of CO₂ a trading system was set up. Every country and industry got a certain amount of CO₂ credits. If a company has a shortage of CO₂, it has to buy credits on the market. At the moment (March 2009), CO₂ goes around for approximately €12 per ton. However, in the coming years, emissions rights will be redivided, but less credits are available.

This means more CO₂ has to be bought and, therefore, production of steel becomes more expensive. Right here lies an opportunity and the (possible) added value of iron and steel slag. The Iron and Steel Industry emits 646 Mt CO₂ per annum⁶⁾ and taking into account the value of CO₂ on the market there are possibilities for CO₂ sequestration investments. As already discussed GGBFS is a substitute for cement and for clinker in cement. Figure 3 shows the reduction of the tonnages of CO₂ emission by using GGBFS in cement.²⁾

Another approach to reduce the CO₂ emissions in the steel industry is to sequester CO₂ in slag. In this case, the free lime (CaO) and the di- and tricalciumsilicates will carbonate. At the moment, a lot of research is done on carbonation of natural magnesiumsilicate rocks and Electric Arc Furnace slag, as has been presented at the 2nd *International Conference on Accelerated Carbonation for Environmental and Materials Engineering* in Rome, October 2008.⁸⁾ This conference showed that many universities and institutes all over the world are doing research and even prototyping carbonation installations. One of the lead scientists in this field is Prof. Lackner from Columbia University. He wrote an interesting article⁹⁾ about ways to sequester CO₂: carbonation of minerals is mentioned as the most stable form of sequestering CO₂.

Slag minerals like calciumsilicates and free lime and dolomite can be carbonated. These minerals can bind about 25 slag wt% of CO₂. Looking at the amount of steel slag produced in Europe annually, 16.8 million tons, this means in the ideal situation if all slag is carbonated, 4.2 million tonnes of CO₂ can be sequestered. For this purpose flue gasses can be used, as demonstrated by K.J. Reddy *et al.*¹⁰⁾ of the University of Wyoming, USA. He used flue gas from a coal power plant in Wyoming. In this case, fly ash was used to carbonate, but the mechanism is the same. To accelerate the maturing of steel slag, CO₂ can be used. Research on the improvement of slag quality in regard to pH reduction and leachability has been done by the ECN institute in The Netherlands and Corus Steel B.V. Dr. S van der Laan *et al.*¹¹⁾ described how the pH value of the fluid slightly improved after carbonation tests, although it was not sustainable enough. There was no improvement in leaching behaviour of Vanadium. (Dr. R. Comans, Prof. Polettini *et al.* and Prof. Van Gerven *et al.* describe other observations in this area, as published in these Proceedings).

Best Available Technology

At the end of the last century, the EU demanded a reference document with the best available technique in regard to environment, health and safety for every industry. This also applied for the iron and steel industry. The first BREF document is being revised now.¹²⁾ The intention of the BREF document for slag is to give guidelines how slag is produced, treated, processed and utilised according to these Best Techniques. It is a guideline, although Member States see it as law, as is the case in the Netherlands.

Waste Framework Directive¹³⁾

For slag, the Waste Framework Directive (WFD) is of major importance. Until recently, slag was automatically considered as waste, without any discussion. Many papers are available about this and other related topics. A good paper on waste management in the light of the WFD was written by N. Hatscher.¹⁴⁾ It shows many problems and restrictions for, *e.g.*, reusing slag. However, after many years of discussion, the WFD has been amended and the term By-product has been added. For slag, the following Articles of the WFD are of importance:

- *Article 3*: “waste means any substance or object which the holder discards or intends or is required to discard”.
- *Article 4*, the Waste hierarchy (Ladder of Lansing), describes in what order wastes are to be discarded. In some countries this is applied in a very stringent way, like in the Netherlands. Therefore, slag is not landfilled in Holland.
- New to the WFD is *Article 5*, By-products. This article opens the way for slag becoming a (by)-product and obtain more value. The rules for being regarded as a by-product instead as a waste are as follows: further use is certain; direct use without any further processing other than normal industrial practice; production is an integral part of production process; further use is lawful, *i.e.* with regard to all relevant product, environmental and health protection requirements.
- *Article 6*, End-of-waste status, regulates when a substance is classified as waste, ceases to be waste.

An important paragraph in this *Article 6* is:

1. Certain specified waste shall cease to be waste... when it has undergone a recovery, including recycling, operation and complies with *specific criteria to be developed* in accordance with the following conditions:
 - The substance or object is commonly used...
 - A market or demand exists.
 - The substance or object fulfils the existing legislation and standards.
 - The use of the substance or object will not lead to overall adverse environmental or human health impact.

The criteria shall include limit values for pollutants where necessary and shall take into account any possible adverse environmental effects of the substance or object.

The lines in italics indicate that new criteria still have to be developed. Those developments are done by different Technical Committees and the Joint Research Centre. The JRC published the final report on End of Waste Criteria in 2008.¹⁵⁾ This report describes in detail what the criteria are and what requirements have to be met. The eye catcher in this report is the non-existence of environmental requirements for aggregates as a product, but nonetheless the adverse effects should be avoided. To achieve this, the report refers to developed legislation or regulations of the Member States to protect soil and groundwater. These could be used as criteria. However, each Member State has its own leaching procedure and requirements. New leaching requirements can be developed, but are time consuming. Another way to determine the End-of-Waste status is by adopting the inert waste criteria used in the Landfilling Directive. Most Members use this criterion. The JRC has also published a final report of a Study on the Selection of Waste Streams for End-of-Waste assessment.¹⁷⁾ In the published list, iron and steel slag is categorised with ash and incinerator slag. GGBFS is seen as a by-product with a positive value. The other slag types are not mentioned as hazardous. But also here the environmental issues concerning leaching are key issues and will need specific documentation. Discussions with authorities and law makers are important, here and elsewhere in the world. The Euroslag association has had extensive discussions with the authorities in Brussels and wrote comments on the preliminary report of the JRC.¹⁸⁾ In the USA, long discussions with congress are held¹⁶⁾ to get slag accepted as aggregate.

The above discussions make companies very creative in finding new ways of using slag and how to get slag accepted as valuable aggregates. In cooperation with the State Environmental Department, companies in the USA are working on building “Green Highways”. Using slag and other types of materials, new highways are built to prove these materials are Green.¹⁹⁾ Another action in the USA is educating civil engineers at technical colleges and universities.²⁰⁾ All too clearly ‘slag’ is something unknown, therefore unloved. Another example of slag utilised in an inventive way is to clean storm water. B. Bourke *et al.* from Steel Serve Ltd. in Awaiuku, New Zealand describes how different kinds of slag are tested for cleaning degraded water from heavy metals.²¹⁾ In Canada, Dr Aleksandra Drizo from the University of Vermont is doing research on EAF slag as storm water purifier, especially for the removal of phosphorous.²²⁾ The field tests are focused on rejuvenating the slag.

Harmonisation Committees

Within the EU, many committees are active on a wide range of subjects. Those committees are called Technical Committee (TC). One of these TCs is the *TC 145 Aggregates*. This TC is divided in several subgroups. One of these groups, TG 13 is concerned with Dangerous Substances. The scope of this TC is to generate standards in

regard to release of certain dangerous substances from aggregates. Aggregates in this case are:

- Natural aggregates;
- Ironmaking slags;
- Steelmaking slags;
- Defined of manufactured lightweight aggregates;
- Recycled aggregate from material previously used in construction.

The standards to be developed for these aggregates will be compared with geologically similar deposits to make the approach more robust. The so-called Regulated Dangerous Substances (RDS) that can be released from those natural and artificial aggregates are compared and identified. For slag this means in practice that the relevant RDS are Mineral oil, metals like V, Cr, Zn, Pb, Mo, As, Hg, Cd, and certain other inorganic substances such as chlorides and sulphates. As soon as the standards are established Classes of Release Potential have to be defined. *TC 351* is active in this area. They developed the concept of Without Testing (WT), Without Further Testing (WFT) and Further Testing (FT) for materials or substances. For the RDS to stay within the WT/WFT area, 3 classes have been defined based on the Dutch column percolation test:

- Below the European regulated limit (probably Dutch);
- Declared class with maximum release, but above minimum;
- No requirements for non regulated markets.

The mentioned WT, WFT/FT procedures were published in a technical report in October 2008.²³⁾ If an aggregate is put on the market bound or unbound, natural or artificial, it has to be tested. For bound aggregates, if there is no leaching it goes Without Testing. Process control is inevitable and a Factory Production Control (FPC) certificate is necessary to supply. If, however, the aggregate is unbound, potential leaching is present. If the Initial Type Assessment (Risk assessments, exposure scenarios *etc.*) shows no leaching of RDS, the material can be used Without Testing. If, however, there is potential leaching of RDS, a so called Initial Type Test (ITT) is required. The ITT involves several tests to determine what and how much RDS is released. Many statistical procedures and a lot of effort are involved. In Figure 4 a simplified outline of the WT, WFT, FT principle is given.

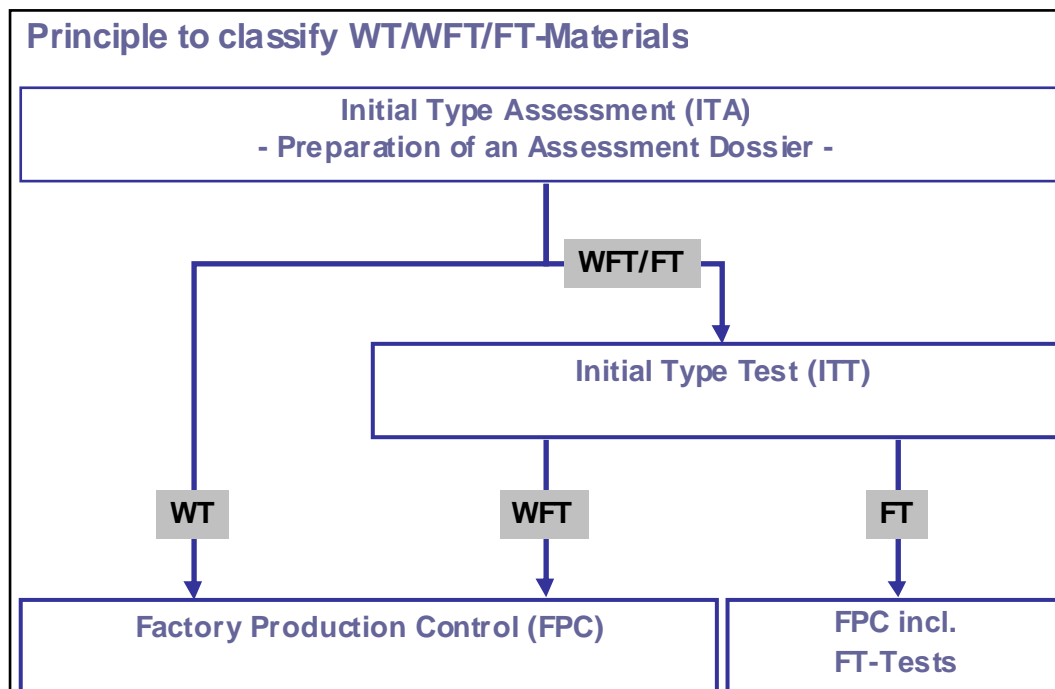


Figure 4: The classification principle for WT/WFT/FT of aggregates²⁾

Looking at the above described procedures a resemblance with the REACH legislation cannot be denied. In all cases, extensive tests, risk assessments and exposure scenarios are required. If the REACH registration document is filled in properly, a large amount of the above required information is already available.

Conclusions

Looking at the European and Member State laws and legislation, this really is a jungle. Companies have to find their way through all the paperwork and different interpretations. These seem all trade barriers, although the EU devotes herself to level the barriers. Nonetheless, slag is still a wanted aggregate for very different purposes. Slag is rock like and has similar properties, sometimes even better. As mentioned before, GGBFS is very valuable for the cement and concrete industry. GGBFS is transported all over the world: from Japan to the USA, from Finland to Spain, from Holland to Ireland *etc.* The material is sold as a product and important for reducing CO₂ emissions. Air cooled BFS is used for road construction in Europe, but mainly in the USA. In its broken form it is very useful as an unbound slag mixture for road construction. BOF slag is used as hydraulic material, armour stone, sand replacement, asphalt aggregates (high PSV values), in cement industry *etc.* Improvement of the stability (volume expansion due to free lime) gives added value to slag. New angles of use are needed. CO₂ sequestration is one good opportunity. Using slag in water

purification is another. EAF slag is stable and very suited for asphalt aggregate, road foundation *etc.* Secondary Steelmaking Slag can be used in mixtures and stabilised with for instance Borax.

Whatever the utilisation of the slag may be, complying with EU, Member State, US law, State law or whatever legislation is a precondition. However, these do not have to be a barrier, but can give opportunities as well. Important is thorough research, inventive new ideas, incorporate the authorities in projects and educate engineers and civil servants. In the USA, governmental institutes and bodies are cooperating with slag aggregate producers in road works and water filtration. In Europe, trajectories are known as well, but hard to start up. Valorisation of slag depends on the ingenuity of the slag producers, slag processors and slag users. There are many barriers, but also many opportunities and reasons to add value to the slag. This starts in the furnace through process control (*see also Session on Hot Stage Slag Processing in this Proceedings*). Cool down the slag in the proper way. Handel it afterwards and improve it if possible during the process. Slag is a product with a future.

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Session 4

Slag cooling and energy/metal recuperation

Visionary Outlook towards Dry Quenching of Slags and Heat Recovery

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Abstract

The steel industry is a high energy consuming industry. The liquid hot metal is produced mainly in blast furnaces, adding coal and other reducing agents as well as some slag forming agents to achieve the right quality of the hot metal and a liquid slag with the desired composition. In the steelmaking process, solid scrap and iron ore are added to the hot metal while carbon in the melt is decreased by blowing oxygen. Again slag formers are added to perform metallurgical work and to take up impurities. After finishing the steelmaking process, steel is cast into billets or slabs and rapidly cooled into solid. The slags from iron and steel production are also cooled down into the desired products. From both solidifying processes the heat is generally not used. In this article a vision on the possible use of parts of the heat from the solidifying slag is described.

Introduction

The steel industry is a high energy consuming industry. Considerable amounts of coal, coke oil, oxygen etc. are necessary to produce steel from natural resources. In Fig. 1 an overview on the input of energy resources into an integrated steel mill is shown.¹⁾ From Fig. 1 it is clearly recognisable that about one third of the primary energy input is used as reduction enthalpy.

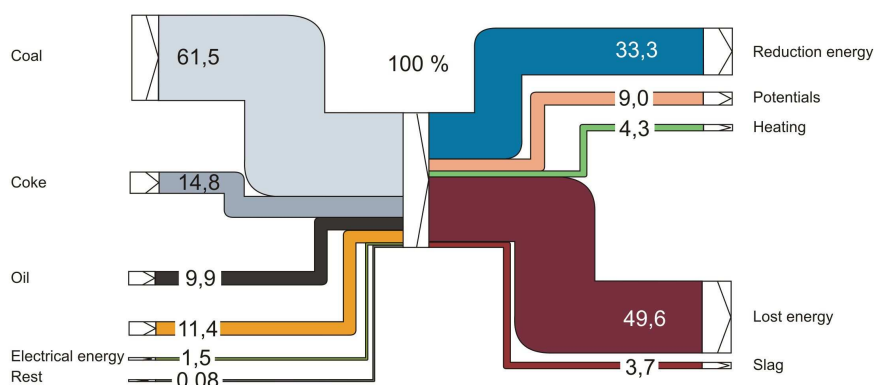


Figure 1: Energy balance of an integrated steel shop (Werner *et al.*¹⁾) [data in %]

This part cannot be influenced or reduced. The main part is set free in the form of sensible heat. Only about 4.5% of this sensible heat is already used for heating purposes. Another 9% has a potential capacity, which is technically useable, today. More than 50% of the energy is lost. The reasons are manifold. Most of this waste heat is at low temperature level, rendering its use too complex. A direct use of heat from cooling steel and slag to solid material is also difficult to handle. However, about 7% of the lost waste heat stream is within the solidifying slags. There seems to be an additional potential for heat recovery. Slags are tapped at high temperatures into granulation devices or slag beds due to the required properties of the products. This might be a prospective possibility for heat recovery and is another step towards more energy efficiency in the steel industry.

Table 1: Enthalpy of iron and steelmaking slags (estimated values for further calculations)²⁾

Slag type	Enthalpy of liquid slag	
	MJ/kg	kWh/kg
Blast furnace slag	2.093	0.581
BOF-slag	2.198	0.610
EAF-slag	2.303	0.639

Slag properties

Each process step on the way to final steel has its own slag type. The main classification is made according to the process step where the slag comes from, *e.g.* blast furnace slag (BFS), BOF slag, and secondary steelmaking slag, which are the slag types of all follow-up process steps to casting. In Table 1 enthalpies of some liquid slags are given.²⁾ With these data the heat content of liquid slags can be calculated. According to Table 1 the amount of heat carried out of the blast furnace per tonne of iron, assuming a specific slag volume of 280 kg/t HM, is about 0.59 GJ/t HM or 0.163 MWh/t HM.

For steel production the specific slag amount is about 100 kg slag/t liquid steel. Hence, the heat content in the slag is about 0.22 GJ/t liquid steel, respectively 0.06 MWh/t liquid steel. Provided that 100% of the energy in the slags is used, about 0.16 MWh/t liquid steel is bound in the liquid slags at temperatures between 1450°C and 1650°C. These figures look very small, but considering the huge amount of slags that are produced every day, the energy from the production of a steelwork manufacturing (about 6 million tonnes of steel) can be compared to the production of a coal combustion power station of 120 MW. Under these circumstances it is worth to think about heat recovery from slag.

Blast furnace slag

Blast furnace slag amounts to approximately 2/3 of the total amount of slag generated in an integrated steel works. To start with, the first investigations on heat recovery have been carried out for this type of slag. The slag is tapped from the blast furnace together with hot metal. The tapping temperature is between 1450°C and 1550°C, depending on the requirements of the steel shop. As soon as the slag is separated from the hot metal in the siphon, the slag cools down. At the end of the slag runner the temperature lost is about 50°C to 100°C. This temperature drop influences the properties of the liquid slag. Due to the increase of viscosity with decreasing temperature of the slag the flow patterns gets worse (Table 2). Even at high temperatures of 1500°C blast furnace slag is very viscous compared to other metallurgical slags.

Table 2: Influence of temperature on properties of liquid blast furnace slag

Temperature decreases	Influence on casting conditions, product quality	Influence on heat recovery
Viscosity increases	Unfavourable casting conditions, tendency to build up long filaments	↓
Tendency to form solids	Loss of material, no uniform flow conditions	↓
Heat conductivity is increasing	Additional heat loss, temperature drop	↓
Less temperature difference for granulation	Less glass content in the product low product quality	

The temperature influence on the viscosity of blast furnace slag is shown in Figure 2. The viscosity data are calculated by a viscosity model developed by FEhS-Institute.³⁾ It is based on the models of Urbain and Riboud.⁴⁾ On the contrary to the model of Urbain, the FEhS-Institute model uses Weymann constants depending on the composition and ratio of CaO/SiO₂. By this, the model is notably applicable for iron and steel slags. In Fig. 2 the dependency of the viscosity from temperature and the slag CaO/SiO₂ ratio is described.

The main point, however, is the quality of the blast furnace slag product. Glassy granulated blast furnace slag is used as main constituent in blast furnace slag cement. About 65% of the blast furnace slag generated in Europe is used for this purpose.⁵⁾ The quality demands on the product are high. It is necessary to meet these quality demands to guarantee the market for the slag. The demands on granulated blast furnace slag are: high latent hydraulicity which can be obtained by a glass content higher than 98%, and a basicity $\text{CaO/SiO}_2 > 1$.

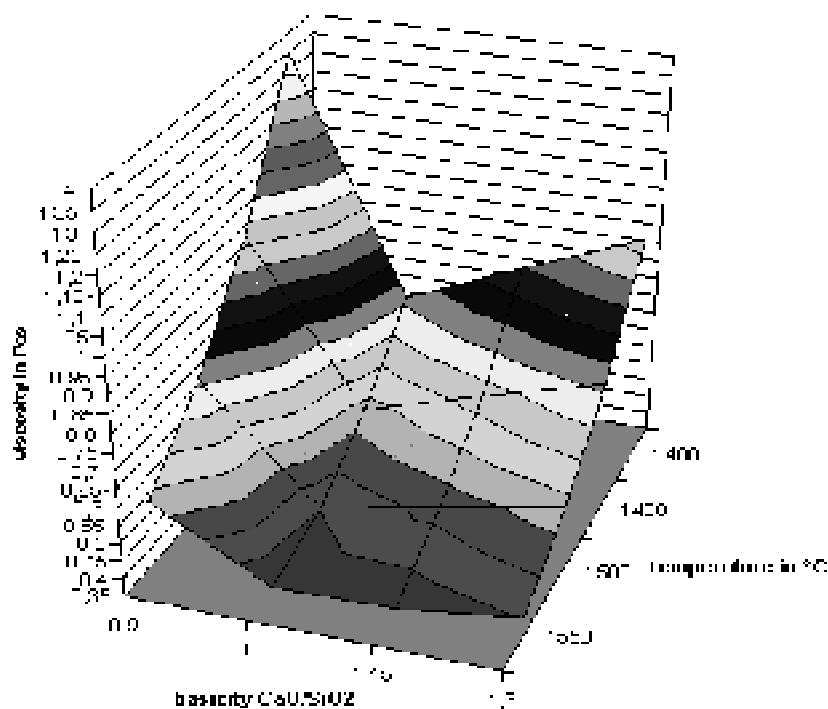


Figure 2: Viscosity of blast furnace slag depending on basicity CaO/SiO_2 and temperature

Alternative cooling and heat recovery processes must not lower the quality of the product that is produced by water granulation, today. This is a must: otherwise granulated blast furnace slag will come into competition with flue gas dust from coal combustion power stations. This demand forms a constraint for the possible heat recovery processes. A glassy slag is obtained by rapid cooling of the liquid slag, so that crystallisation is inhibited. These conditions are given during the slag granulation process. The slag is cooled with a surplus of cold water to assure the high cooling rate, necessarily. The disadvantage of this process is, however, that the product is wet and has to be dried prior to grinding it into cement.

In Figure 3 the energy demand of the different process steps to produce cement from granulated blast furnace slag is represented. The necessary energy for drying the granulated slag prior to grinding is depending on the surrounding conditions, *e.g.* transport, about 15 % of the total energy demand, see Fig. 3.⁶⁾ That becomes more clear by calculation of the energy demand without grinding, since also clinker has to be ground, Fig. 4. Besides transport the grinding energy demand is high. This high energy demand makes it necessary to think about other techniques for rapid cooling and heat recovery at the same time.

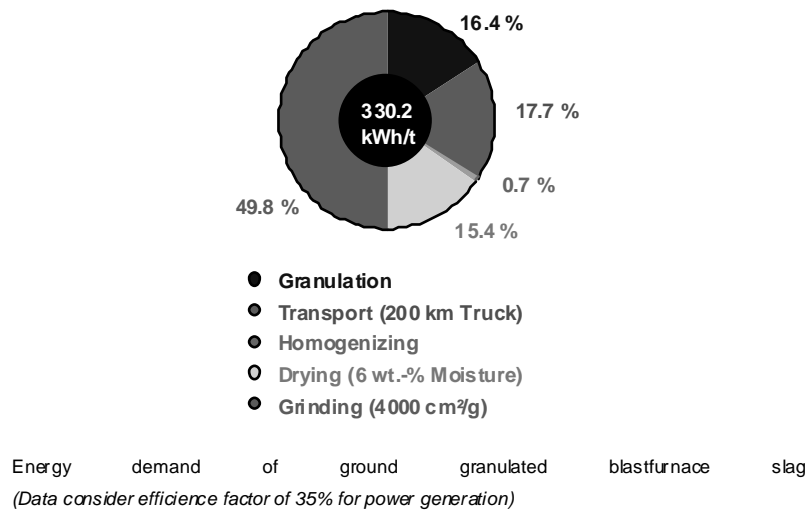


Figure 3: Energy demand to product cement from blast furnace slag

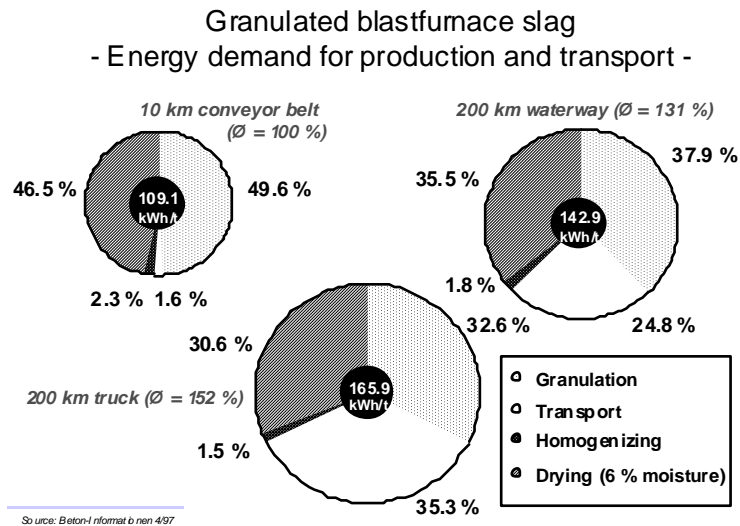


Figure 4: Effects of the use of granulated blast furnace slag as main constituent in cement on the energy demand for cement production

Heat recovery from blast furnace slag

In the past some proposals have been made to recover heat from solidifying slags. A comprehensive overview on the processes developed in the seventies of the last century is given in the thesis of K.H. Lindner.⁷⁾ Parts of this thesis are published.⁸⁾ As far as processes for heat recovery from blast furnace slag have been described, these processes all suffer from the fact that the product is not as glassy as required for a good product for cement production. The main problem of heat recovery is in the temperature and heat conductivity of the slag, Fig. 5. It is necessary to rapidly dissipate the heat from the solidifying slag in order to get glassy material. Experiments have shown that insufficient heat dissipation increases the crystalline amount in the slag. Since the slag

has miserable heat conducting properties, it is necessary to produce small particles and extract the heat by high temperature gradients. For example, in the water quenching process increasing water temperatures can result in lower glass contents in the granulated slag product and thus worse cementitious properties of the material. Based on these facts new technologies have been published recently.⁹⁻¹¹⁾ The main idea of these processes is to achieve a rapid cooling of the slag by pouring it onto cooled steel plates in thin layers. By this a high heat flux into the metal can be achieved. Together with the inventor, FEhS-Institute has carried out some first tests to confirm the expected results. However, these tests show that the materials quality depends on the thickness of the layer and the temperature of the steel plates. This has to be considered when constructing a cooling installation.

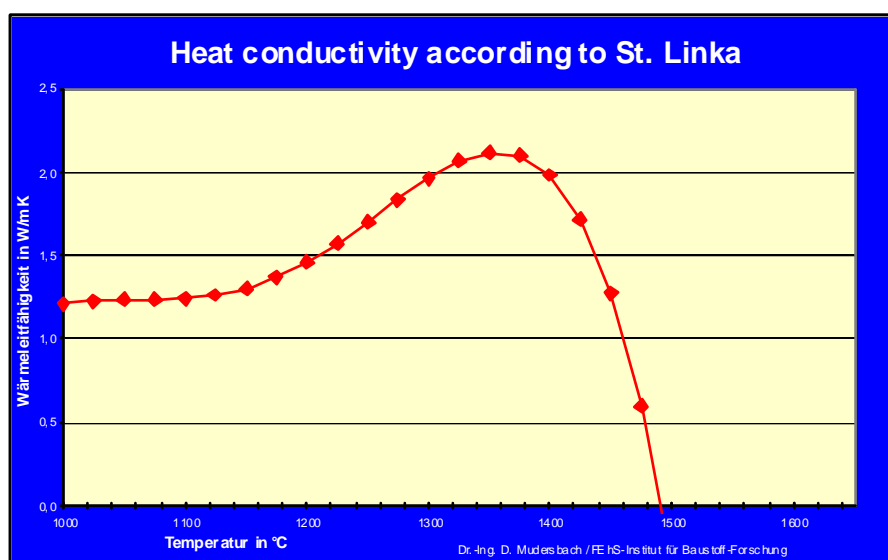


Figure 5: Typical heat conductivity of blast furnace slags

Under the consideration of the slag product quality, it is necessary to think about possible ways and techniques to recover this heat. As shown in the visionary statements before, considerable amounts of heat can be recovered. However, the typical properties of liquid slag have to be paid attention to. Slag at tapping temperature is liquid and has high temperatures between 1450°C and 1650°C, but the heat capacity of the slag is critical. Viscosity changes occur very quickly with decreasing temperatures. Thus the flow patterns of a slag are instable. As soon as there is a solid phase around a liquid slag particle, the heat cannot be conducted outside from the inner part. This is the main difference on the solidification of slags compared to metals. And if there is a slag lid, the remelting of the lid is nearly impossible.

The preliminary remarks give a very short overview on the requirements necessary to achieve a material with sufficient quality for further use as cement constituent. After having solved these technical problems additional heat recovery is possible during solidification by heat radiation. As soon as the slag is solid, it can be carried into a shaft to cool it further by convection cooling, for example by air. The hot air can be used for steam production or used directly to produce hot blast for the blast furnaces.

As already mentioned in the introduction, the heat content in blast furnace slag is about 0,163 MWh/tonne HM. Concerning the production of 10.000 tonne HM per day, the heat in the slag is 2.800 MWh/day. If only 50% of the slag's heat can be recovered, the usable heat from only the blast furnace slag is 10% of a 700 MW coal fired power station. If the heat will be used as heating source for the hot blast of a blast furnace, the effects are much higher, since there is no additional loss by heat exchanging.

Steel slags

The use of heat from steel slags is not limited by demands on glass contents. Due to the higher basicity of the slag, it is nearly impossible to solidify steel slags glassy; the slag is always crystalline. However, tests on rapid cooling show advantages according to the volume stability of slags. BOF slags have problems as regards to volume stability due to the free lime content in the slags. Rapid cooling of the slag avoids the precipitation of free lime from the disintegration of tricalciumsilicate into dicalciumsilicate plus free lime. Thus it can be observed that the amount of free lime in the slag is low, and the slags are volume stable. This constitutes a major advantage for the latter use.

Some EAF slags have the tendency to disintegrate during cooling according to the conversion of β -dicalciumsilicate into γ -dicalciumsilicate at elevated temperatures. This conversion can be avoided by rapid cooling. This is used in some EAF steel works already. The slag is tapped on steel slabs and immediately cooled with water, avoiding disintegration. This is the idea for further investigations on heat recovery by using the slab as boiler. Thus part of the heat content can be used. Further cooling in a shaft will deliver additional energy.

Conclusions

During iron and steel production a lot of energy is consumed. The liquid products, *i.e.* steel and slag, have to be cooled to solidify. This solidifying and cooling heat is mostly unused and lost into the atmosphere or in the cooling water with low temperature levels. In the future it will be necessary to think about heat recovery. The first step should be the investigation of heat recovery from solidifying slags. This step does not directly influence the production patterns of the primary products, being iron and steel.

As shown in the visionary statements before, considerable amounts of heat can be recovered. However, the typical properties of liquid slag have to be paid attention to. As soon as there is a solid phase around a liquid slag particle, the heat cannot be conducted outside from the inner part. This is the main difference on the solidification of slags compared to metals.

Finally, heat recovery from slags will be available in the future. However, before solving problems of heat recovery, an appropriate cooling system to produce solid materials from the different slag types has to be developed. Several proposals have been presented in the past. However, none of these proposals produces slags that meet the required product qualities. The newly generated slag product must have the same or even better product qualities compared to the products that are produced today. To summarise, heat recovery from slags presupposes good knowledge of the behaviour of the slag and its properties during solidification. A slag melt is different to a melt of metal.

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Energy Recuperation from Slags

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Abstract

The sensible heat of slags produced in steel works can be expected to be a valuable source of energy in the future. At present, however, the sensible heat of molten slags is not recovered in practice. In order to develop an effective heat recovering from molten slags, the technology for dry granulation processes of slags, heat exchange processes and chemical heat recovery processes are discussed.

Introduction

To meet the demand of the recent environmental and energy issues, many efforts have been carried out in steelmaking industries. However, very few areas remain where CO₂ emissions or energy consumption can still be decreased, considering that, from a thermodynamic point of view, the iron and steelmaking process has already been optimised to a great extent. One of the few possible areas to further improve these processes consists of the heat recovery from molten slags. The sensible heat in molten slags is a very useful heat source as its temperature is over 1673 K. High temperature heat sources mean that the efficiency of the heat recovery process is greater and the heat can be utilised in a greater variety of processes.

For every 4 tonnes of hot metal produced, about 1 tonne of molten slag (about 1773 K) is discharged, releasing subsequently about 1.8 GJ/t-slag of sensible heat on cooling, which is currently not recovered. For example, the Korean steel industry produces more than 10 million tonnes of slags each year with waste heat up to 18 PJ/y. The combustion of 1 tonne of carbon produces about 33 MJ of heat. Thus, the waste heat of 18 PJ/y is equivalent to that produced in the burning of about 2.0×10^6 tonnes of carbon:



This carbon combustion produces about 7.3×10^6 tonnes of CO₂, which is equal to 10% of the current CO₂ production of the Korean steel industry. Namely, if the sensible heat of molten slags were effectively recovered, the amount of CO₂ emissions from Korean steel industry can be reduced by about 10%.

Thus, the recovery and use of such high-grade waste heat is a very attractive way to meet the demands of environmental and energy issues. However, further improvement is still necessary to make it economically attractive. Heat recovery from molten slags is not a recent concern. Several attempts have been already carried out to develop heat recovery processes.¹⁻⁸⁾ Few industrial processes, however, have been established for practical use. In this paper, the required technology for the effective heat recovery from slags is discussed.

Previous works on heat recovery from molten slags

Dry granulation

For the development of the effective heat recovery process from slags, we must take into account the following unfriendly properties of slags.

- (1) The viscosity of slags very quickly decreases with decrease of temperature or their fluidity is significantly decreased.
- (2) Their latent heat and heat conductivity is quite small (about $1 \text{ Wm}^{-1}\text{K}^{-1}$ or lower).
- (3) Generally, slag contains soluble gas which makes a blow hole during the solidification process. This gas hole may create a good adiabatic layer so that the inside can remain liquid.

For the improvement of heat recovery efficiency, it is essential to break up slag into *small* droplets for fast cooling and solidify the droplets with gas. This process is commonly referred to as “dry granulation”. Dry granulation processes are already industrially applied, especially in the non-ferrous field.¹⁾ In these industrial processes, the heat recovery was not attempted. Potentially, however, high grade heat may be recovered from slag droplets or solid granules so that several pilot scale attempts have been attempted.¹⁻⁹⁾

Dry granulation processes can be carried out by a several means such as air blasting, rotary drum and spinning cup. In a pilot scale process, heat is often recovered from solid granules in a fluidised or packed bed to produce hot gas. Some proposed processes are summarised in Table 1.

Table 1: Proposed processes for heat recovery from slags

Process	Developer	Scale	Slag	Efficiency
Air Blast	NKK & MHI (1984)	Plant	BF & BOF	45 %
Single Drum	IHI & Sumitomo Metal (1980)	Plant	BF	60 %
Twin Drums	NKK & MHI (1984)	Plant	BF	40 %
Spinning Cup	British Steel & Univ. Of Nottingham (1985)	Design	BF	60 %

In these attempts, about 40 to 60% of slag heat was recovered in the form of hot air of over 873 K. These values suggest that the sensible heat recovery from slags is quite promising. However, further improvement of the heat recovery efficiency and higher gas temperatures are required for economically attractive heat recovery processes.

Thermal channelling

Proposed several processes applied a packed bed system to recover the heat after the granulation of slags. Packed-bed processes are common in chemical and metallurgical processes. The advantage of packed bed processes is the high potential of the heat and mass transfer efficiency. However, it is also known that some processes, particularly the energy-intensive ones, can be inefficient in terms of heat transfer. A hot moving bed of solids cooled by a cold gas is an inherently unstable system and divides into steady state regions of vastly differing mass velocity and temperature. Heat transfer inefficiency can be attributed to this non-uniform gas flow distribution and is called “thermal channelling”.

Wonchala and Wynnycky¹⁰⁾ calculated gas temperature distribution as a function of thermal flow ratio of gas and solid, R , as shown in Fig. 1.⁹⁾ It is noted that the gas temperature profiles are very sensitive to R in the vicinity of $R = 1$. The temperature distribution at $R = 1$ is a special case. Theoretically, it is the most efficient operating point for a heat exchanger. It is, however, an unstable condition in practical applications.

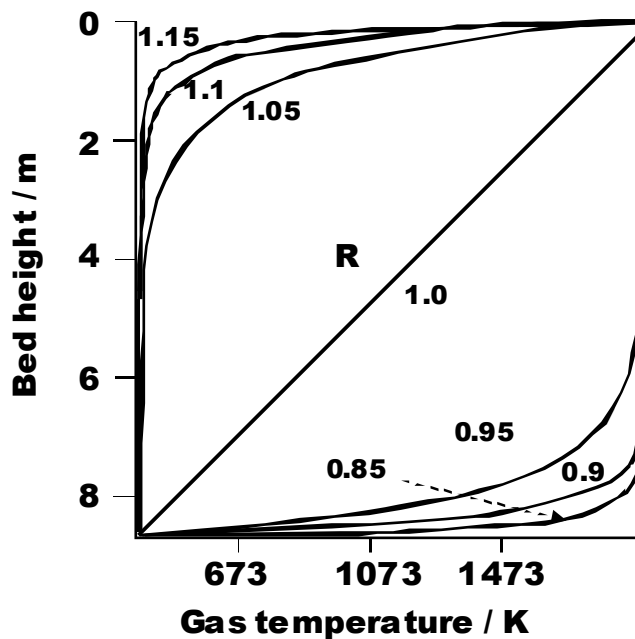


Figure 1: Gas temperature profile for moving bed for various values of R ¹⁰⁾

They also calculated the bed pressure drop in a moving bed.¹⁰⁾ The results are shown in Fig. 2. In the figure, the gas supply pressure, P_L , is plotted against R over a wide range of R at two different packing densities, ε , and fixed $P_0 = 126$ kPa. Intriguingly, the flow ratio is not unique for a fixed P_L . At a constant ε , there are 3 possible values of flow ratio, shown as R_1 , R_2 and R_3 in Fig. 2. The details of calculation can be found elsewhere.⁹⁾ These results represent a most important property of hot moving beds being cooled by counter-currently flowing gas.

For the effective heat exchange operation, the operating condition must be carefully selected to avoid the unstable conditions. However, several parameters, such as bed height, particle diameter and temperatures of solid and gas cannot be changed that much. Potentially we may not avoid the thermal channelling. The concurrent moving bed system is widely used in an industrial practice. However, we still need some practical expertise for the effective sensible heat recovery from molten slags. As an alternative approach for the heat recovery, a fluidised bed process might be used. However, the relatively high temperature and size of slag granules may create another difficulty.

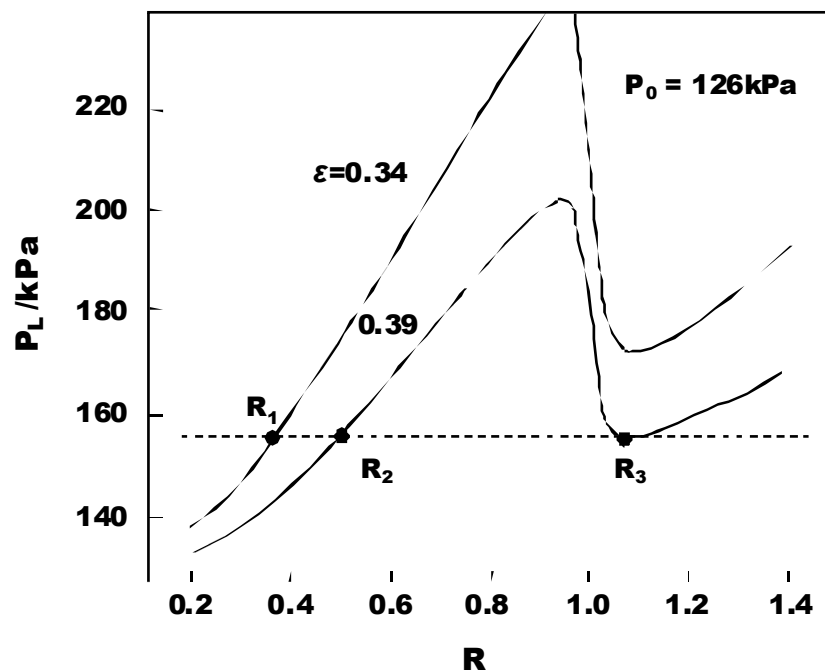


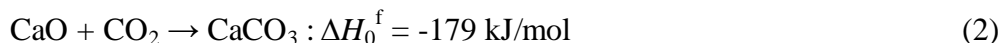
Figure 2: Gas pressure for a given thermal flow ratio⁹⁾

Chemical heat recovery

Along with the sensible heat recovery from molten slags, chemical heat recovery from slags is also possible. Steelmaking slag contains a high fraction of CaO that exothermically reacts with CO_2 to form carbonate. This carbonation reaction makes slags an attractive and plausible way for sequestration of CO_2 . It is called “mineral CO_2

sequestration process” and a lot of attention has gone to this process (*see also Session 1 in this Conference Proceedings*).¹¹⁻¹⁴⁾

The purpose of these investigations is to capture CO₂. Just as mentioned before, however, the carbonation reaction of CaO is a strong exothermic reaction. The energy released in this reaction is substantial, and is about half of the value of the carbon combustion reaction of (1).



Namely, the carbonation reaction of CaO is very attractive for the recovery heat process application as well as for CO₂ sequestration. Therefore, the chemical heat pump processes based on the CaO carbonation reaction have been extensively investigated. However, the interest of this research lies in maintaining the reactivity of CaO during the heat pump cycles since the CO₂ capture capacity of CaO gradually decreases after the series of carbonation/calcination cycles. Our purpose is the heat recovery from slags so that the enhancement of the carbonation reaction rate is important, and not the repetitive use of CaO.

The carbonation reaction with CO₂ proceeds very slowly at room temperature. The reaction accelerates with increase of temperature. However, if temperature is raised too much the chemical equilibrium shifts so that free CO₂ is favoured over CaCO₃. By comparing the free energies of the reactants and reaction products, we can estimate the highest allowable temperature that allows binding of CO₂. This temperature is a function of the partial pressure of the CO₂ in the reactor. In Fig. 3, the equilibrium p_{CO_2} in the reaction (2) is shown.

The equilibrium p_{CO_2} increases with temperature. For example, the p_{CO_2} in BF top gas is about 0.2 atm. It means that CO₂ in BF top gas cannot react with CaO at more than 1073 K. Thus, the carbonation reaction at high temperature is not preferable. Slags actually consist of several minerals. The equilibrium p_{CO_2} or temperature can be easily calculated in a similar fashion for direct carbonation of common minerals existing in BF or BOF slags. Fig. 4 shows the free energy of formation of calcium carbonates from the minerals as a function of temperature, for two different pressures.¹³⁾ If the free energy difference is negative, which requires low temperatures, the reaction proceeds towards the carbonates, whereas at high temperatures the free energy difference changes sign and the reaction proceeds towards the oxides. Thermodynamic data are available for a number of calcium bearing minerals, and have been used to estimate the maximum carbonation temperatures.

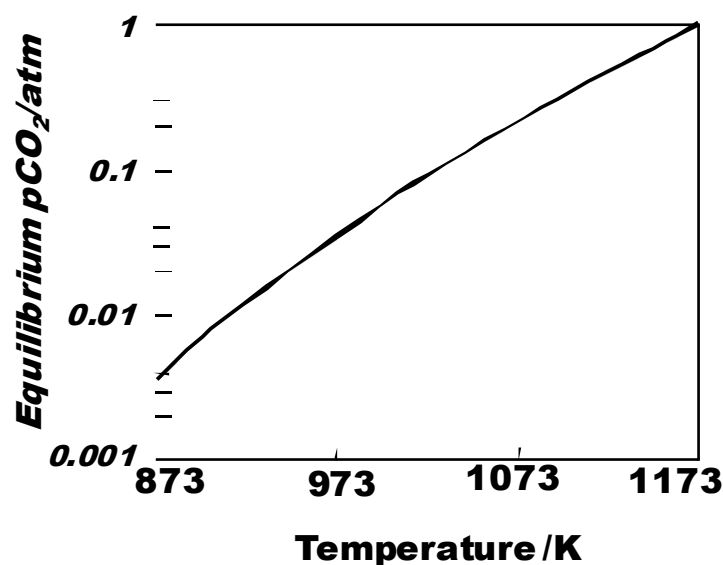


Figure 3: Equilibrium partial pressure of CO_2 over CaO

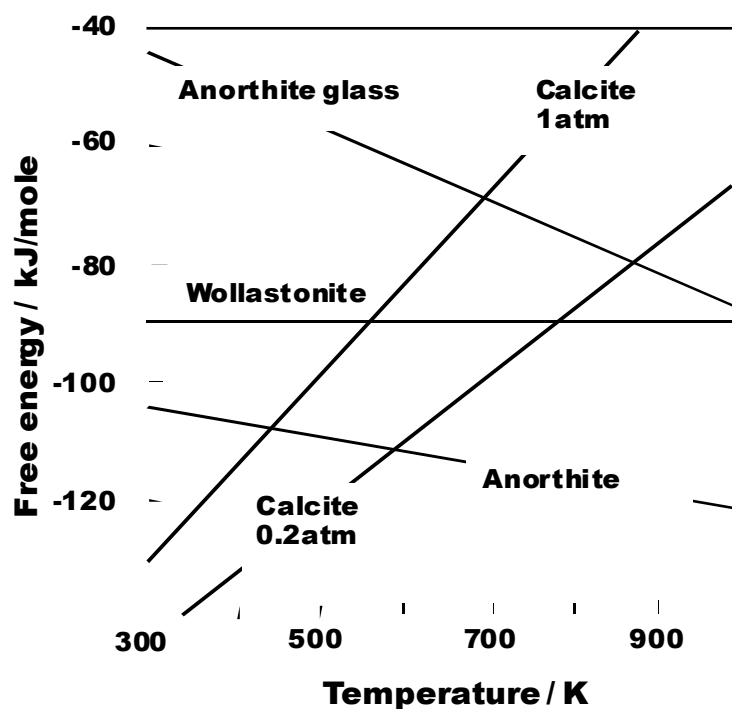


Figure 4: The free energies of formation of carbonates and Ca bearing minerals.¹²⁾
 Calcite: $CaCO_3$, Anorthite: $CaO \cdot Al_2O_3 \cdot 2SiO_2$, Wollastonite: $CaO \cdot SiO_2$

As already mentioned, the exothermic nature of the carbonation reaction implies that all the processes are net energy producers. Therefore, the main constraint for a cost effective implementation is the rate of the carbonation reaction. Since the carbonation cannot be carried out at high temperature, the effective and possible way to enhance the

reaction rate of carbonation of CaO bearing minerals is simply to increase the reaction area of reacting slags or the use of fine slag powder. It means that the granulated slags need further grinding treatment for the fine powder production.

As the slag granulates comminution is energy-intensive, we must pay attention to the fact that the energy required to grind the slag should not exceed the energy recovery benefit.¹⁵⁾ The accurate characterisation of the comminution energy to apply the chemical heat recovery from slags is required. The development of effective comminution process can be the key technology for the effective chemical heat recovery from slags. The practical and effective process for the heat recovery from fine slag powder can be achieved by using a fluidised bed system, and is already well established.

Concluding remarks

The sensible heat recovery from molten slags can be effective at higher temperature. Its efficiency will decrease with temperature. Conversely, the chemical heat recovery from slags is applicable at less than about 700 K. Thus, we can possibly maximise the efficiency of the heat recovery from molten slags by the optimal combination of the sensible heat recovery and the chemical heat recovery processes.

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Metal Recovery from Slags

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Abstract

In the present study new sustainable processes for recovery of metals from slags with a microwave treatment, as developed by the author's group, are reviewed. Although some steelmaking slags could be easily heated by 2.45 GHz microwave irradiation, the effect of carbon addition was considerably large. Furthermore, it also caused carbothermic reduction of Fe_2O_3 , P_2O_5 and CrO_x , which enabled the recovery of iron, phosphorous and chromium from the steelmaking slags. The carbothermic reduction behaviour of both synthetic and industrial steelmaking slags by microwave irradiation was investigated. The larger the carbon equivalent (C_{eq} , defined in text), the higher the fractional reduction of iron and phosphorous became. An increase in SiO_2 content of the slag led to a considerable improvement of reduction for both iron and phosphorous due to increases in the fluidity of the slag and in the activity coefficient of P_2O_5 in the slag.

Introduction

Due to the recent economic development of the Asian countries, the annual amount of steel production in Japan gained as much as 120 million tons, which inevitably generates more than 40 million tons of slags. While most of the blast furnace slags are effectively utilised as resources for cement and roadbeds, etc., steelmaking slags (more than 10 million tons per year) are desired to be used as products with more added value. Also, waste slags contain considerable amount of undissolved CaO , iron oxide, phosphate, etc., which are not well recovered. On the other hand, we import considerable amount of phosphorous as a resource for fertilizers. Hence, more attention has to be paid to the assessment of more effective utilisation of steelmaking slags.

Microwave processing is a fast and efficient way of heating materials which have high dielectric losses or high electrical conductivities. Morita *et al.*^{1,2)} utilised microwave processing in the treatment of incineration ash and investigated the possibility of stabilisation of hazardous elements. The incineration ash was melted in a crucible under microwave irradiation. The experimental setup is shown in Figure 1. Samples were cast into glassy blocks as shown in Figure 2, where a reduction reaction had occurred to produce an iron droplet in oxide melts.

Then this idea was translated to the treatment of steelmaking slags. Using the same apparatus, the heating behaviour of steelmaking slags and the possibility to recover iron, phosphorous and chromium by microwave carbothermic reduction reactions, were investigated.^{3,4,5)} In the present paper, most of the studies on metal recovery from steelmaking slags by microwave processing are reviewed.

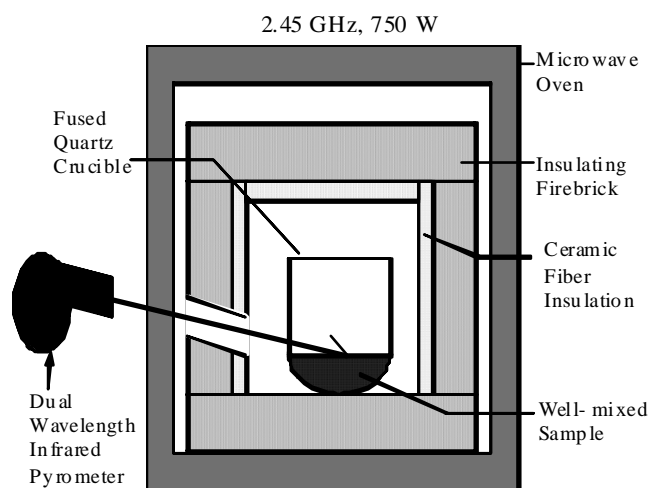


Figure 1: Schematic diagram of the experimental apparatus

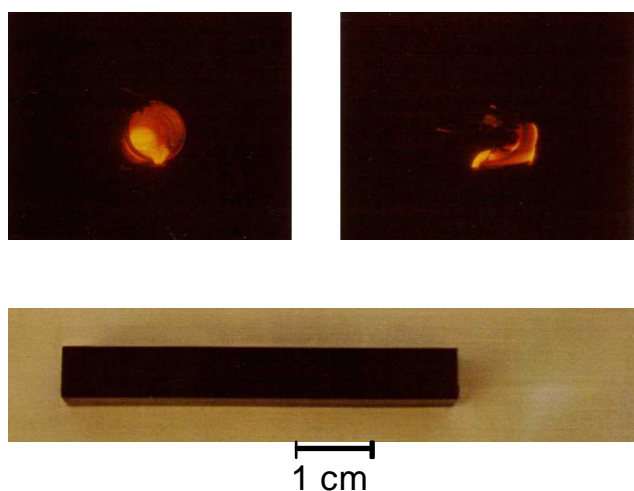


Figure 2: Molten ash and the cast glassy sample

Heating and reduction behaviour of synthetic steelmaking slags^{3,4)}

Firstly, the heating characteristics of the steelmaking slags were clarified. Ten grams of the synthetic $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$ slags were treated in a microwave oven (1.6 kW, 2.45 GHz). Some samples contained phosphorous and carbon as a reductant. Slag compositions were adjusted to $\text{wt\% CaO/wt\% SiO}_2 = 1$ and $\text{wt\% Fe}_2\text{O}_3 = 67$ or 47. As

shown in Figure 3, most slags were heated up to higher than 1273 K in 3-4 minutes, which confirmed the microwave absorbance of steelmaking slags. The heating rate strongly depended on $\text{Fe}^{3+}/\text{Fe}^{\text{total}}$ fraction and when $\text{Fe}^{3+}/\text{Fe}^{\text{total}}$ equals 0.166 and 0.153, it showed the largest for the slags with wt% Fe_2O_3 67 and 47, respectively. This was found to be due to the largest amount of CaFe_3O_5 phase, whose dielectric loss was as high as that of Fe_3O_4 , that was contained in each slag.

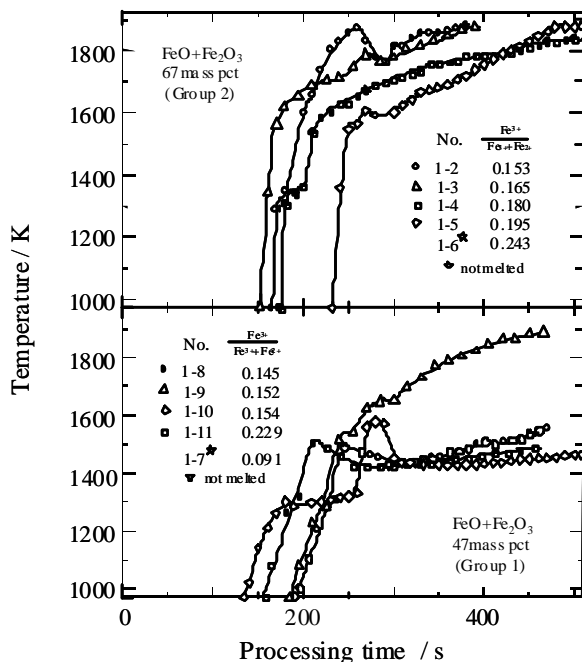


Figure 3: Change in temperature of synthetic steelmaking slags with processing time

On the other hand, joule heat is generated when microwaves are irradiated to conductive materials with large specific surface area, such as powders and fibers. When graphite powder was mixed with ground slags, they were effectively heated and Fe-C alloy was formed at the bottom as shown in Figure 4, regardless of slag composition. There was a positive relationship between C equivalent (C_{eq} = the ratio of the mixed carbon to the amount theoretically required for the reduction of Fe_2O_3 to pure metallic iron) and heating rate, and the recovery ratios of iron and phosphorous increased with C_{eq} . When C_{eq} was 1.5, the recovery ratio of iron was as high as 95%. (Figure 5)

Figure 6 shows the relationship between C_{eq} and the material balance of phosphorous after the microwave treatment for 3 min after the temperature reached 1873 K. Unknown amount is presumably due to the vapourisation of phosphorous because the temperature at the surface of graphite particle would be locally higher than the average temperature measured in the experiment. Extraction of phosphorous from the reduced Fe-C melt was also verified using carbonate fluxes.

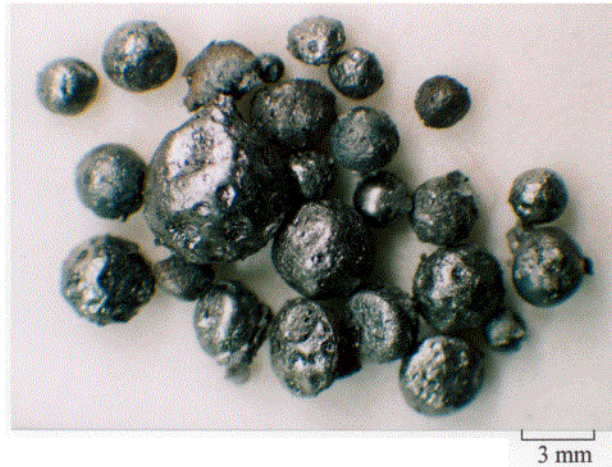


Figure 4: Particles of Fe-C-P alloy reduced from slag by microwave carbothermic reduction (Processing time = 7 min, Carbon equivalent = 1.5)

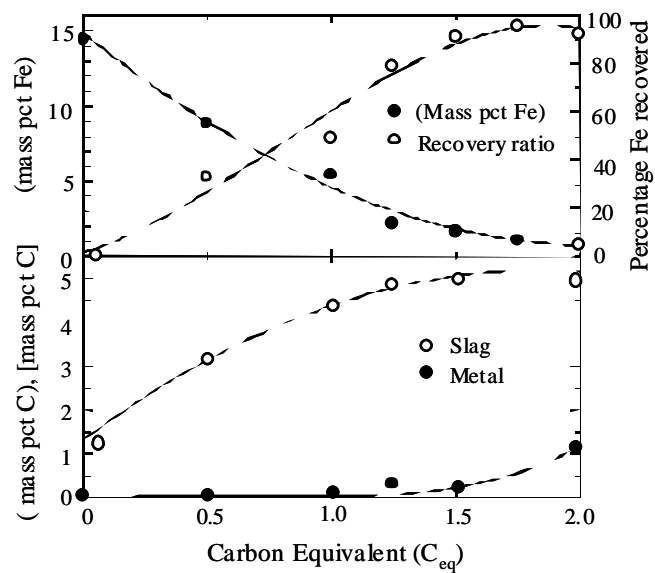


Figure 5: Effect of carbon equivalent on the reduction behavior of the synthetic slags

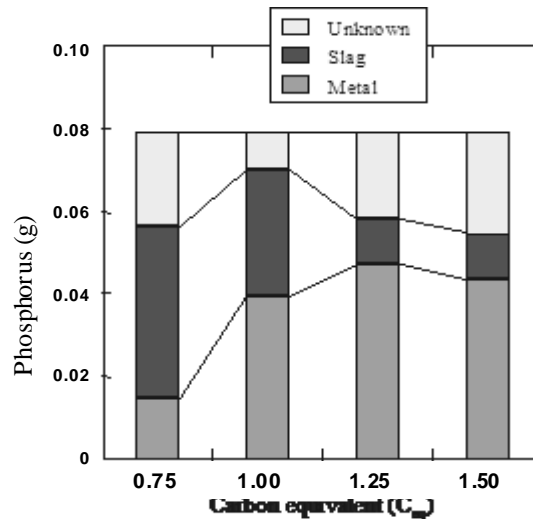


Figure 6: Effect of carbon equivalent (C_{eq} ; horizontal axis) on the material balance of phosphorous

Reduction behaviour of industrial steelmaking slags⁴⁾

Based on the results obtained from the experiments of the synthetic slags, the reduction behaviour of the industrial steelmaking slag was investigated in similar conditions. The slag composition is shown in Table 1. The changes in iron, phosphorous and carbon contents of the slag and metal and iron reduction ratio for $C_{eq} = 1.5$ against processing time are plotted in Figure 7. With the increase in processing time, both the iron and phosphorous content of the slag decreased and the iron reduction ratio increased. This was consistent with the decrease in carbon content of the slag, which was depicted in the top diagram of Figure 7. Finally, the iron content of the slag was as low as 4 wt% and the reduction ratio reached about 60%. On the other hand, the phosphorous content in the reduced metals reached as much as 9 wt%, although the phosphorous content of the slag decreased only by 50%. Figure 8 shows the time dependence of material balances of iron and phosphorous in metals and slags after the microwave processing. Both iron and phosphorous in slags were gradually reduced into the metallic phase with processing time, and the fractional reduction of iron was more significant than that of phosphorous. The unknown amount for both elements is considered to be due to uncollectable fume and dust generated during the reaction, and probably also due to gasificating dephosphorisation for phosphorous.

Table 1: Chemical composition of the steelmaking slag (in wt%)

(T.Fe)	(CaO)	(SiO ₂)	(MnO)	(MgO)	(P ₂ O ₅)	(Al ₂ O ₃)
11.7	41.9	26.6	5.80	5.20	4.00	3.20

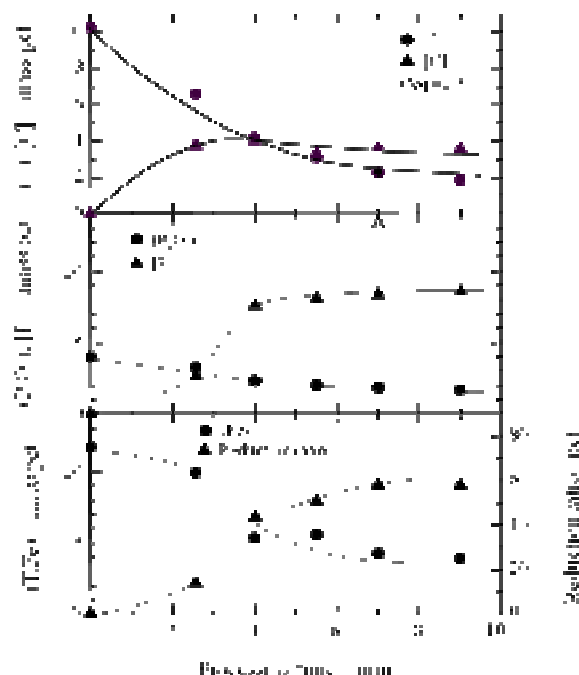


Figure 7: Changes in iron, carbon and phosphorous contents of slag and metal and iron recovery ratio with processing time

Figure 9 shows the effect of the carbon equivalent on the final composition of the slags and metals after 7 minutes of microwave processing. As expected, the extent of reduction was considerably affected by the amount of reductant. The reduction ratios of iron and phosphorous increased with increasing C_{eq} , and they reached about 70 and 50%, respectively, when C_{eq} was 2.5. The iron and phosphorous contents of the slag decreased with increasing C_{eq} , and did not change when C_{eq} exceeded 1.5. This is also compatible with the behaviour of carbon shown in the top diagram of Figure 9. The carbon content in metal increased up to 4.0 wt%, and then decreased slightly after C_{eq} was higher than 1.0, whereas the residual carbon in slag increased with C_{eq} .

As seen in the middle diagram of Figure 9, the phosphorous content of the slag decreased with C_{eq} , and was lowered to 25% of the initial content at $C_{eq} = 2.5$. Phosphorous content of the metal increased with increasing C_{eq} , showing that the reduction of phosphorous was affected by the amount of reductant. The distributions of iron and phosphorous between slag and metal for seven minutes of microwave treatment were plotted as a function of carbon equivalent in Figure 10. It is obvious that the increase in C_{eq} brings about increases in the distribution of iron and phosphorous in the metallic phase, which is consistent with the results shown in Figure 9. Also it can be seen in Figure 10 that the loss of phosphorous was significantly higher than that of iron. As mentioned in the results for synthetic slags, it is considered to result from the gasifying dephosphorisation during microwave processing.

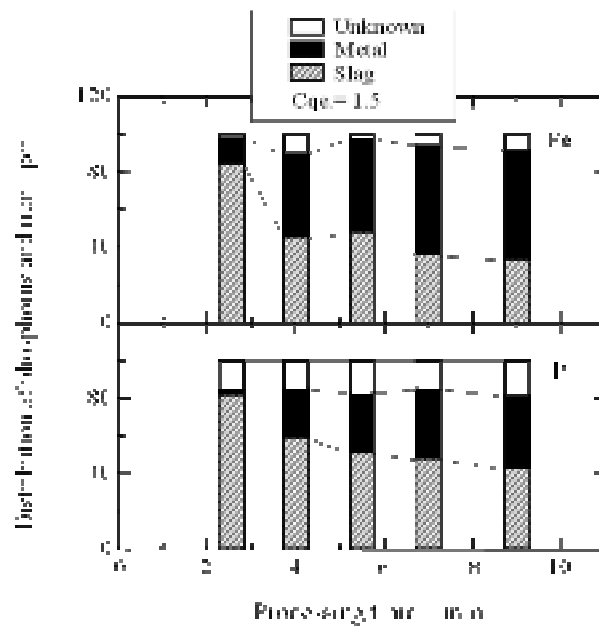


Figure 8: Material balances of iron and phosphorous between metals and slags as a function of microwave processing time

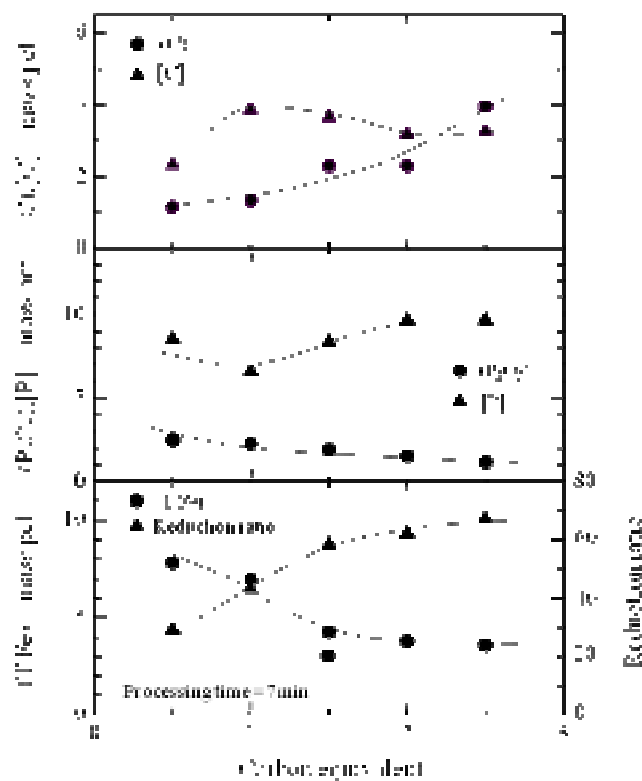


Figure 9: Effect of carbon equivalent on the reduction behaviour of iron and phosphorous in slags

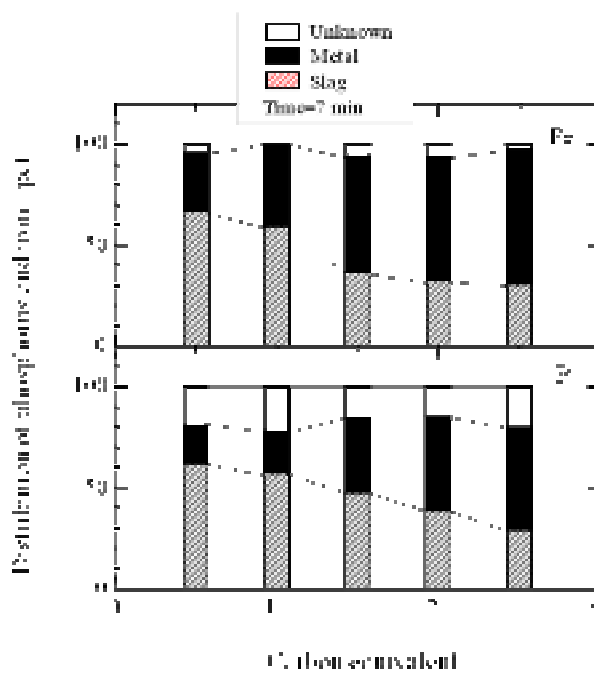


Figure 10: Material balance of iron and phosphorous between metals and slags as a function of carbon equivalent

For studying the effect of the SiO_2 content of the slags on the reduction behaviour, the experiment with extra 10 wt% SiO_2 addition to the industrial steelmaking slag was conducted. The processing time and carbon equivalent were fixed at 7 minutes and 1.5, respectively. Figure 11 shows the difference in the distribution of iron and phosphorous after microwave processing with and without the addition of SiO_2 . The material balance of iron and phosphorous indicated that SiO_2 additions led to a considerable improvement of the fractional reduction for both iron and phosphorous. Especially, phosphorous was reduced more effectively, and its reduction ratio reached as much as 74%, and only about 10% of phosphorous remained in slag, the rest is considered to be removed into the gas phase. These results can be interpreted by the change in the slag composition after microwave processing as shown in Figure 12.

The original steelmaking slag composition moved towards the lower iron oxide region and reached the $2\text{CaO}.\text{SiO}_2$ saturated two phase region during processing. This leads to a decrease in the fluidity of the slag, thus causing the decrease in the reduction rate. However, in the case of the extra 10 wt% SiO_2 addition, slag remained as a single liquid phase during the full processing time, which is favourable for the smooth mass transfer in the reduction behaviour. Moreover, the activity coefficient of phosphorous oxide (P_2O_5) in the molten slag is significantly dependent on the slag basicity. A decrease in the slag basicity brings about increases in the activity coefficient of P_2O_5 . Thus, the fractional reduction of phosphorous oxide was improved more than iron oxide when an extra 10 wt% SiO_2 was added to the steelmaking slag, as shown in Figure 11.

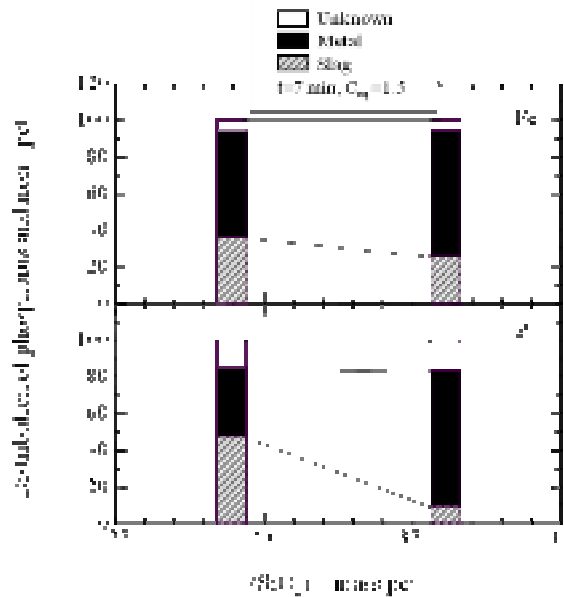


Figure 11: Effect of SiO₂ content in the slags on the reduction behaviour of iron and phosphorous from slags

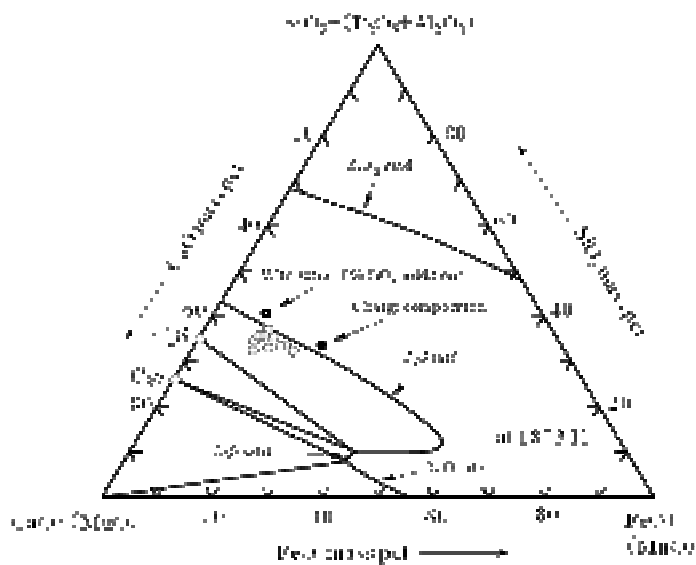


Figure 12: Change in slag composition after microwave processing

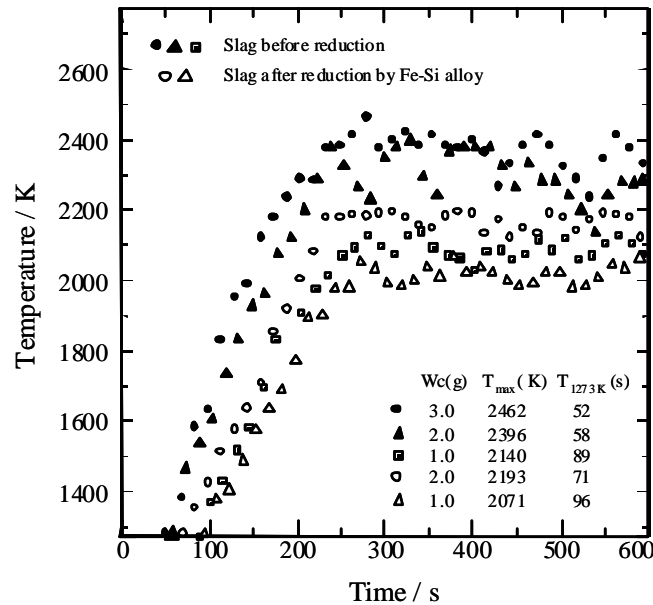
Reduction behaviour of industrial stainless steelmaking slags⁵⁾

Two types of typical industrial stainless steelmaking slags were subjected to microwave carbothermic reduction. One is the slag “before reduction”, namely, the slag sampled before reduction of chromium in the stainless slag. The other is the slag “after reduction by Fe-Si.” Their compositions are listed in Table 2.

Table 2: Chemical composition of two types of stainless steelmaking slag

	(wt%)				(CaO)/(SiO ₂)
	(T.Fe)	(T.Cr)	(Al ₂ O ₃)	(TiO ₂)	
Before reduction	8.9	18.7	2.9	-	1.51
After reduction	0.7	2.9	2.2	0.5	1.33

Figure 13 shows the temperature behaviour of the slags with various amount of carbon addition. Both types of the slags were effectively heated and the maximum temperature of some slags was higher than 2400 K. Compared with ordinary steelmaking slags, the heating rate was considerably faster, probably due to the existence of chromium oxide although this is not clarified.

**Figure 13:** Change in temperature of stainless steelmaking slags with processing time

The reduction behaviour of chromium and iron in the slags “before reduction” and “after reduction” are shown in Figures 14 and 15, respectively. The chromium and iron contents in both slags decrease with processing time, and their reduction yield increase correspondingly. In case of the slag “before reduction”, more than 90% of chromium and iron was reduced, whereas the reduction yield of iron in case of the slag “after reduction” with $C_{eq} = 2.5$ reached only 20 %. In spite of the thermodynamic priority in the reduction of iron oxide to chromium oxide, the final contents of iron and chromium in both slags were found to be in the same order, 0.7 wt% Fe and 1.5 wt% Cr for the slag “before reduction”, and 0.5 wt% Fe and 0.5 wt% Cr for the slag “after reduction”.

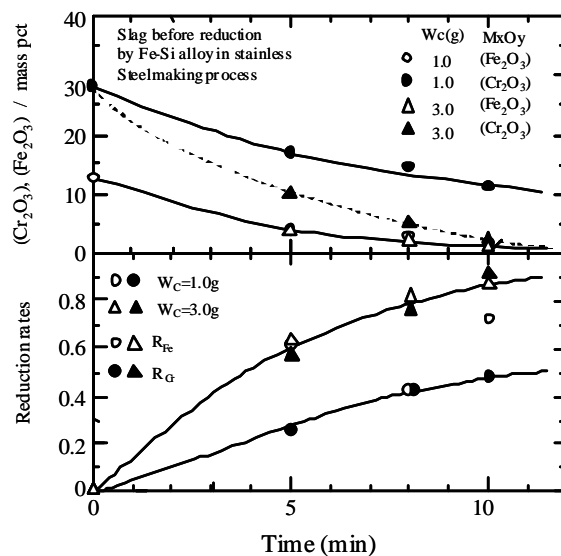


Figure 14: Changes in iron and chromium contents (as Fe_2O_3 and Cr_2O_3) of stainless steelmaking slags “before reduction” and their recovery ratios with processing time

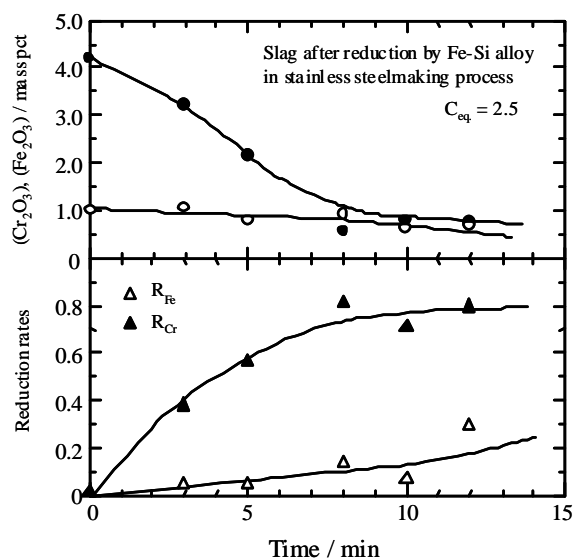


Figure 15: Changes in iron and chromium contents (as Fe_2O_3 and Cr_2O_3) of stainless steelmaking slags “after reduction” and their recovery ratios with processing time

Conclusions

Examples of microwave (2.45 GHz, 1.6 kW) application to the recovery of metals from steelmaking slags were reviewed in the present paper. Possibilities of the recovery of iron, phosphorous and chromium from steelmaking slags were clarified. The results obtained are summarised as follows:

1. The heating behaviour of the synthetic $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$ slag was considerably influenced by the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio. Microwave energy was absorbed most efficiently when the value of $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ was around 0.16. When $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ in slags was far from this value (0.16), the heating rate decreased considerably.
2. The experimental results of the synthetic slags show that the slags were heated up to over 1873 K and a lump of Fe-C alloy with a diameter of 2-8 mm was formed. Recovery ratio of iron from slags increased with larger C_{eq} , and it reached 90% at $C_{eq}=1.5$.
3. In the experiments with the industrial slags, the recovery ratio of iron reached about 70% at $C_{eq} = 2.5$. The phosphorous in the slags decreased with C_{eq} , and it was lowered to about 25% of the initial content when C_{eq} was 2.5.
4. An increase in SiO_2 content of the slag led to a considerable improvement of the reduction for both iron and phosphorous due to the decrease in the fluidity of slag and the increase of the activity coefficients of P_2O_5 .
5. Chromium was recovered from stainless steelmaking slags. The residual chromium content of the slag “after reduction” was as low as 0.5 wt% after 10 minutes microwave irradiation with $C_{eq} = 2.5$.

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Session 5

Slag applications

Slag Valorisation in China: an Overview

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Abstract

The hot stage treatment processes for BF slag and BOF slag and their application are introduced in this paper. The focus lies on some new processes developed in China, such as the HK process for BF and BOF slag granulation, and the BSSF process for BOF slag granulation. The status of granulated BF and BOF slags application in metal recovery, cement production and the related national standards are also reported. Finally, the research activities in valuable elements recovery from special BF and BOF or copper slag are reviewed.

Introduction

The Chinese metallurgical industries and especially the steelmaking industry have been embracing great progress in light of the economic growth that China is experiencing. The crude steel production of China in 2008 is 500 million tons, which is 37.7% of the total world crude steel production.¹⁾ On average, the production of blast furnace slag is 346 kg/t hot metal. For steelmaking slag this value was 137 kg/t steel in 2002. The total slag quantity (novel and accumulated) is quite huge. Furthermore, the valorisation of ironmaking and steelmaking slags in China is more difficult, considering that some complex iron ores, containing either titanium, vanadium, rare earth elements, or boron, are used. The typical composition of some BF, EAF, BOF slags, titanium or rare earth containing BF slags and vanadium bearing BOF slag are listed in Table 1 and Table 2, respectively.

There is about 0.5% and 5% metal iron entrapped in, respectively, the blast furnace slag and BOF slag. It is the most valuable iron resource in steelmaking slags. Other components such as calciumsilicates can also be utilised as fluxes or cement materials etc. after suitable treatment. The titanium oxides contained in blast furnace slag are valuable components as well. Furthermore, many non-ferrous metallurgy slags contain iron oxides and other valuable elements. Nowadays, facing the rising prices of energy and resources, it is getting increasingly difficult to develop metallurgical industries without taking into account the constraints on the environment and resources. The Chinese metallurgical industries are seeking a sustainable way of developing, which will lead to more efficiency in resource utilisation, waste reduction, clean production

and a better life quality. The valorisation of slags in China has progressed. As we can see in Table 3, the recycling ratios of blast furnace slag and steelmaking slag gradually increased.²⁾ In this paper, the recent developments on molten slag treatment, valorisation processes and scientific research are briefly reviewed.

Table 1: The composition of ironmaking and steelmaking slags in China (w t%)

Slag Type	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	FeO	MnO	TiO ₂	P ₂ O ₅
BOF	13~19	1.4~5.3	34~45	7.2~13.6	6.5~16.0	12~21	0.8~5.7	0.6~1.1	1.2~1.5
EAF	22~24	7.7~11.0	25~35	4.9~6.6	1.2~6.2	13~17	1.3~3.4	0.7~6.8	0.3~0.5
BF	32 ~35	11.6~14.4	35~39	9.0~10.6	0.9~3.1	—	0.1~1.2	0.5~1.6	0.01~0.02

Table 2: The composition of titanium/rare earth bearing BF slags and vanadium bearing BOF slag in China (w t%)

Slag Type	SiO ₂	Al ₂ O ₃	CaO	MgO	F	Fe ₂ O ₃	FeO	MnO	TiO ₂	V ₂ O ₅	C	RE _x O _y	P ₂ O ₅
Titanium bearing BF slags	19~32	13~17	20~31	7~9			0.2~1.9	0.3~1.2	6~31	0.06~1.0	4.1~5.2		
Rare earth bearing BF slag	32.04	7.96	38.2	7.63	5.55		0.45	1.75	0.98	1.23		3.86	
Vanadium bearing BOF slag	10.1	2.2	48.6	9.8		5.33	19.1	2.15		1.7			0.95

Table 3: The utilisation ratios of ironmaking and steelmaking slags in China (w t%)

Slag Type	1995	2000	2001	2002	2006	2007
BF slag	84.32	86.18	89.10	89.52	92.72	91.1
BOF slag	79.36	82.14	77.20	86.92	89.75	88.82

The hot stage processing for BF and BOF slags

The hot stage processing for BF slags

In China, different processes are used to granulate the BF slags. The main processes are OCP, RASA, INBA, TYNA and SG-MTC. These processes involve pouring the molten slag through a high-pressure water spray in a granulation head, located in close proximity to the blast furnace. The slag undergoes accelerated cooling under controlled water flow, thus forming vitreous solidified slag sand. After granulation, the slag/water slurry is typically transported to a drainage system, consisting of horizontal filtering basin (the OCP process), a vertical filtering hopper or a rotating de-watering drum (the INBA process). In several cases, the slag/water slurry is transported to a separation tank prior to water drainage (especially RASA process). In case of the TYNA process, the

molten slag is granulated first by a water cooled rotating wheel mechanically and then further cooled by water. Granulated slag sand is mainly sold to the cement industry for cement production. RASA process was adopted in 1980s by Baosteel for the No. 1 Blast furnace (4063 m³).³⁾ INBA and TYNA methods are popular in large scale integrated iron and steel works. INBA process was developed by SIDMAR and Paul Wurth in 1981. Due to its reliability, low sulphur emissions, and limited water consumption, the INBA process was first introduced in 1991 by Baosteel for No. 2 Blast furnace (4063 m³).⁴⁾ After that, Wuhan, Ma'an Shan, Benxi, and Taiyuan Steel companies adopted the INBA process. Three sets of TYNA processes were introduced from Russia by Tangshan Steel in 1998 for its 2560 m³ blast furnace.⁴⁾ The improved TYNA process (the so-called HK method) was operated in Taiyuan Steel for a 1650 m³ blast furnace.⁵⁾ In case of the SG-MTC method, the slag slurry after water quenching is filtered by a screw lift. It was designed by Sougang Group and MTC companies and operated in 2002 for a 2536 m³ blast furnace.⁶⁾

The hot stage processing for BOF slags

About 7 processes are being used in Steel works for BOF slag stabilisation treatment in China.

Pyrolytic Self-slaking process. The hot slag within a temperature range of 300~800°C is poured into a tank with a cover, while water is sprayed into the tank and thus steam will be generated that reacts with the free lime and magnesia in the slag. The slag is stabilised and cracked to powder or small blocks. This process was designed by China Jingye Eng. Corporation Ltd.⁷⁾ The time for one batch treatment is about 12 h. After treatment, more than 60% of the slag grains are smaller than 10 mm, easy to be separated or grounded further and the steel entrapped in the slag can be recovered with a high yield. The metal remaining in the residual slag after magnetic dressing is less than 1%. Free lime and magnesia can be fully slaked. This process was applied in Valin Steel, Special Steel Branch of Baosteel, etc., for more than 15 years. Due to the good stability, wide suitability of the treated slag, and the high recovery yield of steel grains from the residual slag, this process is becoming popular. Anshan Steel introduced a steel slag magnetic dressing line with a productivity of dressing 2.4 million tons slag per year in 1988.⁸⁾ The magnetic component, which is about 40% of the slag, can be separated and recycled to the metallurgical processes. The remaining 60% of the slag is applied as construction material. The ratio and T. Fe content of magnetic components separated from treated slag are listed in Table 4.⁹⁾

The newly built Bayuquan steel works of An-Ben Steel also adopted this process. The ability of this BOF slag treatment line is 700,000 tons per year, service for 3×260 t BOF.

Layer pouring process. The molten slag is poured to a slag box to be slaked by spraying water on the slag, layer by layer. The treatment needs one week for one cycle. The No. 3 steel works of WISCO has been using this process since 1996.¹⁰⁾ The limitation of this process is its large requirement for space and the dust and steam emissions.

Table 4: The ratio and T.Fe content of magnetic components recovered from steel slag

Items	T.Fe (%)	Grain Size (mm)	Ratio in slag (%)
Steel block	> 80	> 50 mm	10
Steel granule	> 62	10-50 mm	10
Magnetic powder	> 40	0-10 mm	20

Instantaneous slag chill process (ISC). The molten slag is poured onto shallow trays, then chilled to 500°C by an interrupted water stream. The chilled slag will crack due to the stress by water quenching. The cracked slag is then moved to a trolley and cooled to 200°C by water spraying, after which it is dumped into a water pool to be further cooled down. This process was invented by Nippon Steel and imported by Baosteel in 1980s.⁸⁾ This process can only treat slag with good fluidity.

Water-granulation process of steel slag. In China, Ma'an Shan and Jinan Steel use a water-granulation process to treat molten steel slags. Molten slag is quenched and granulated by a high pressure water stream. Ma'an Shan Steel used this process in the 1970s for open hearth steelmaking slag. Jinan Steel has been using this process for BOF slag granulation since 1978 for their 25 ton BOF.¹¹⁾ Their experience proved that the water-granulation process for molten BOF slag is feasible if the slag fluidity can be properly controlled. The grain size of 90% of the granulated slag is less than 6 mm. The phase transformation of dicalciumsilicate and decomposition of tricalciumsilicate can be restrained. To avoid explosion, the flow rate of quenching water and molten slag must be well controlled.

Air-granulation process of steel slag. The molten slag flowing out of the slag pot or the tundish is quenched and granulated by a compressed air jet. NKK Fukuyama works built the first Air-granulation system for steel slag with heat recovery. The merits of this process are its safety, its low water consumption, and the ease to recover part of the heat of the molten slag. Chongqing Steel and China Steel also use the Air-granulation process.¹²⁾ But the Air-granulation system in Chongqing Steel does not yet include heat recovery. About 90% of the molten slag can be granulated to grains with a size smaller than 6 mm.

Wheel-granulation process of steel slag. This is a new process for molten steel slag granulation. It is an improved version of the HK process, which was originally used for BF slag granulation. As shown in Figure 1, the molten slag is poured to a launder and

hit by a turning wheel and simultaneously quenched by high speed water stream, and then further cooled in the water tank. The slurry is filtered and lifted out of the tank. Part of the steam is condensed. Water for quenching is in circulation. The parameters of this process and the properties of the treated slag are shown in Table 5. This process was first applied in Benxi Steel in 2004 for 3×120t and 3×150t BOF. In total 4 units were built. In 2006, Liuzhou Steel built 2 units for their 3×100t BOF.

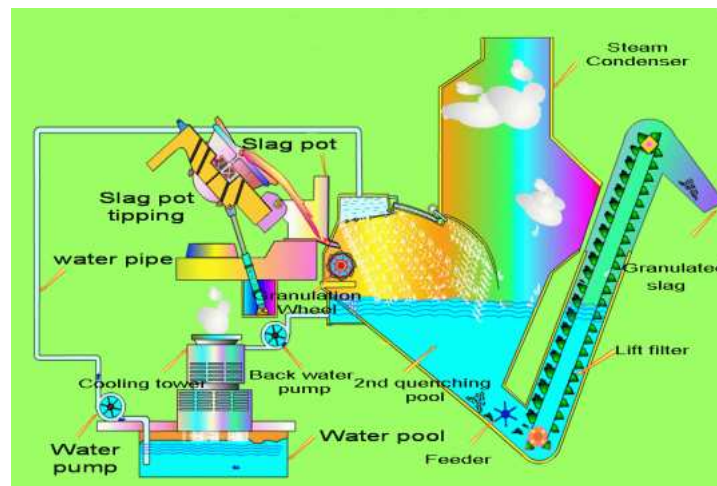


Figure 1: Illustration of the HK steel slag granulation process

Table 5: Operation parameters of the HK steel slag granulation process

An example of slag composition (%)	CaO	SiO ₂	Al ₂ O ₃	FeO	T. Fe	R
	40.6	11.1	3.0	21.0	23.8	3.2~3.5
Temperature of taping slag (°C)	1550~1650					
Water supply (in circulation, t/h)	430~485					
Water pressure (MPa)	0.32~0.38					
Rate of granulation for total slag (%)	80~85%					
Water consumption (t/t slag)	0.657					
Granulation speed (t slag/min)	1.5~3					
Size (mm) distribution of granulated slag	<1	1~3	3~7	7~12.5	>12.5	
	5%	41%	36%	13%	5%	
Water ratio in granulated slag (%)	<10					

Baosteel's Slag Short Flow (BSSF) process. Baosteel began to develop the BSSF slag processing technology in 1995, based on an imported patent from Russian Ural Steel Academe during the Baosteel phase II steelmaking period. The first BSSF slag processing system was built in Baosteel 250 ton BOF works in May 1998.¹³⁾ The BSSF process treats molten slag of high temperature in a special rotating cylinder. Under the co-effect of the mechanical forces by steel balls hitting and water chilling, molten slag is rapidly quenched and crushed. The slaking of free calcium and magnesia in the slag is rapidly completed. The formed BSSF granulated slag is small in size and stable in quality, the slag and steel can be effectively directly separated by magnetic separation.

Figure 2 demonstrates the flow chart of the BSSF process.¹⁴⁾ The molten slag from the steelmaking plant is transported to the slag processing factory by the slag pot trolley.

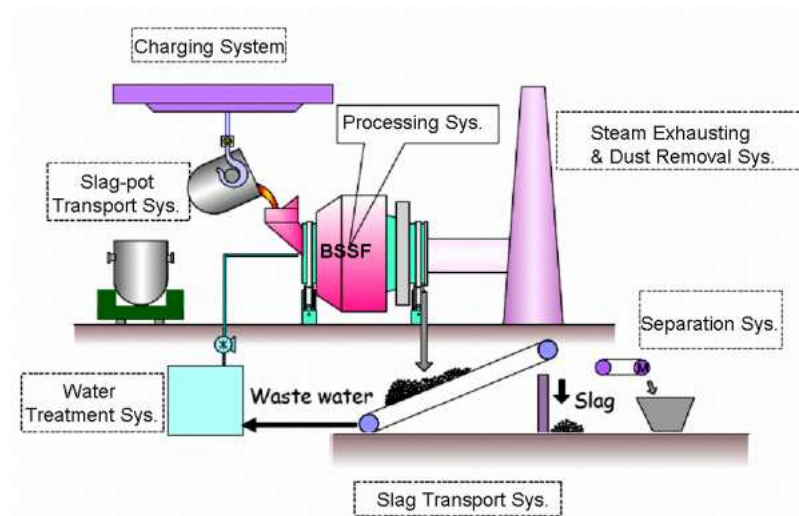


Figure 2: The flow chart of the BSSF process

A crane lifts up and pours the molten slag into the BSSF equipment. A portion of the highly viscous molten slag will be skimmed away by the slag skimmer and put into the BSSF equipment. The molten slag is quenched and fragmented in the BSSF equipment, and solid granulated slag that is normally smaller than 15 mm is discharged. The discharged granulated slag then falls onto a conveyor and is separated via magnetic separation. A spray removes the dust in the steam generated by the slag processing, and the steam is discharged via a smokestack. The maximum treating ability of this process is 3 ton slag/hour. Water consumption is 1 ton/ton slag and 60% of the water is in circulation after being filtered. Free lime in the BSSF treated slag is about 1%. The treated slag is applied in concrete mixture, cement raw material, building materials, fluxes, and sintering additive. Currently, BSSF-A and BSSF-B systems are developed and are applied in Baosteel Branch, Stainless Steel Branch, Ma'anshan Iron & Steel Co. Ltd., Nanchang Steel, Xuanhua Steel and JSW Steel in India.

Slag Valorisation in China

As mentioned above the blast furnace slag is mainly water-granulated and the steel slag is mainly the slaked BOF slag. Therefore, the iron and steel slag valorisation in China primarily implies the valorisation of these two kinds of slags. The valorisation of slags includes other fields as well. In the present paper we are only concerned about large scale valorisation processes.

BF slag valorisation

China had been using granulated blast furnace slag as cement material since the 1950s. The first national standard was issued in 1956. There are six strength grades of slag

cement in the newly issued national common Portland cement standard GB105-2007. The slag cement is divided into two types: A, B. The quantity of granulated blast furnace slag in type A is $> 20\%$ and $\leq 50\%$, that of type B is $> 50\%$ and $\leq 70\%$. Ferroalloy slag such as granulated carbon chrome iron slag, granulated chrome iron refining slag, etc. is prohibited for using in slag cement. Grounded granulated blast furnace slag powder is included in the new standard for slag cement material. Utilisation of slags in the cement industry in a scientific, reasonable and safe way is emphasised by the new standard. The ratio of slag cement in total cement production of China is listed in Table 6,¹⁵⁾ which corroborates that the ratio of Portland blast furnace slag cement in China is quite high. The total cement production of China in 2008 is 1388 million tons.¹⁶⁾ The quantity of granulated blast furnace slag used in cement is very large.

Table 6: Cement varieties ratio of large scale Chinese cement enterprises (%)

Year	Portland cement	Common Portland cement	Portland BF-slag cement	Portland Pozzolan cement	Portland fly-ash cement	Composite Portland cement
1985	4.79	45.99	38.02	1.52	0.9	8.78
1992	7.74	52.3	33.86	1.3	2.28	2.52
2004	5.1	54	36	0.9	2	2

Ground granulated blast furnace slag has a high specific surface area ($420 \text{ m}^2/\text{kg}$), it can be used not only to equivalently substitute $15 \sim 60\%$ of cement in concrete, but also serves as a necessary mineral additive of high performance concrete. The research on the properties and application of ground granulated blast furnace slag in China started in the 1990s.¹⁷⁾ A local standard of “ground granulated blast furnace slag for concrete and mortar” was issued by the Shanghai city government in 1998. This standard was accepted as a national standard (GB18046-2000) and became part of the newly issued national common Portland cement standard GB105-2007. Since then, the application of ground granulated blast furnace slag is becoming mature. The production of ground granulated blast furnace slag on an industrial scale started from 1996. By the end of 2006, more than 20 ground granulated blast furnace slag production lines had been established. Total ground granulated blast furnace slag production was 50 million tons in China. Almost all the ground granulated blast furnace slag is applied in concrete structures. The ground granulated blast furnace slag of Baosteel was successfully applied in the construction of Shanghai levitation road, Lupu Bridge, Shanghai Science Building, and Yangshan deep water harbour. The concrete mixture made by ground granulated blast furnace slag of Baosteel was successfully applied in the Yangzi river tunnel construction.¹⁸⁾ In practical application, the ratio of granulated blast furnace slag substitution for cement is 30% , thereby reducing the cost of concrete construction and the CO_2 emissions due to the cement clinker production.

Steel slag valorisation

The easy way of steel slag valorisation is to re-use it in ironmaking and steelmaking processes. The other ways include its use as road construction material, building material, fertiliser, and landfill material.

Re-use of steel slag in ironmaking and steelmaking processes. The granulated steel slag has been used as sintering flux to recover iron, lime, iron oxides, manganese oxide, and magnesia. The sintering process and sinter quality can be improved. The sinter with steel slag addition is also good for blast furnace operation. Baosteel used steel slag for sinter additives since 1996 and can stably consume 150.000 tons per year by adding 1.2% steel slag in the sinter.¹⁹⁾ The phosphorous enrichment in the hot metal should be noted. By the experience of Baosteel, if 10 kg steel slag is added into 1 ton sinter the phosphorous will increase with 0.0038% and 0.0076% in, respectively, the sinter and the hot metal. So the sinter with steel slag addition cannot be used continuously to avoid the enrichment of phosphorous. Steel slag is also re-used in the steelmaking process. As an example, Baosteel re-uses the decarbonisation BOF slag for hot metal dephosphorisation pre-treatment to produce steel with phosphorous less than 80 ppm with the Baosteel BOF refining Process.¹⁹⁾

Steel slag used as road construction materials. Since the 1970s steel slag has been used as a road base material, civil engineering landfill material or brick material. Most roads with steel slag as a base material were built near steel plants. Several national highways also used steel slag as base materials. After several or 10 years, cracking or ridging was found from these roads. The later strength of slag brick was found low and cracking was observed. The problem was caused by the free lime and free magnesia resulting in the volume instability of the steel slag. By improving the steel slag granulation technology, this problem will be solved. The Chinese Ministry of Construction issued the criterion for construction and acceptance of steel slag-lime stabilised road base materials (CJJ35). The technical criterion for road base layer construction with steel slag mixed material was issued in 1991 by the previous Ministry of Metallurgy (YBJ230). Anshan Steel reported⁹⁾ that their pyrolytic self-slaking steel slag fulfils the requirements of the national standard for road materials and is used to produce three grades of road base materials applying for bottom base layer, base layer and surface layer of highways. Now the national standards for steel slag used as wearing resistant asphalt concrete and the test method of steel slag stability are being written. The soaking expansion rate of steel slag is required to be less than 2%.

Steel slag used in cement. The national standard for steel slag powder used in cement and concrete was issued in 2006 (GBT 20491-2006). Several new standards for steel slag cement applied in road construction cement, brickwork cement, and low heat Portland cement were issued in 2008 (JC/T 1087-2008, JC/T 1090-2008, and JC/T

1082-2008). Many research works on steel slag powder and its applications have been reported in recent years in China. As a mineral additive of cement and concrete, the activity of ground steel slag powder is quite high and close to blast furnace slag.

Li²⁰⁾ studied the composition, structure and properties of steel slag powder and properties of cement and concrete with steel slag powder. His results show that the cementitious properties of steel slag powder are determined by the mineral composition and treating process. The total content of active mineral composition, C_2S , C_3S , C_4AF and C_3A , and the content of $Ca(OH)_2$ determine the cementitious properties of steel slag powder. Cementitious properties of steel slag powder increase with elevated special surface. However, the increase of cementitious properties is not obvious when its special surface is higher than $500 \text{ m}^2/\text{kg}$. Free lime and metal Fe are the main factors which cause volume instability problems of steel slag powder, so their content must be strictly restricted. Content of free CaO must be limited within 3% and content of metal Fe must be restricted to maximum 2%.

Zhu *et al.*²¹⁾ studied the application of WISCO steel slag fine powder, which is used as blending material for several kinds of cement. The experimental results show the powder can be used as blending materials to prepare high strength common Portland cement, composite Portland cement and iron-steel slag cement. The strength of common Portland cement blended with 10% and 15% steel slag powder does not decrease but increase. Its strength grade can reach 52.5 R. If fix the blast furnace slag powder as 15% or 30%, blending with 10%-30% steel slag fine powder, the strength of composite Portland cement can attain 52.5 R, 42.5 R and 42.5. The strength of iron-steel slag cement simultaneously blended with 30% steel slag fine powder and blast furnace slag powder is 42.5. The Portland cement blended only with 35% steel slag fine powder has the strength of 42.5 R. The stability of steel slag fine powder blended cement was confirmed by the high pressure steam test. It fulfils the national standard up to 45% of the blending ratio. The hydrating heat of steel slag fine powder blended cement can be decreased significantly, which makes large volume concrete structures possible. Using steel slag powder in cement industry is a good solution because the quantity of slag consumption is large. Consider that the steel slag cement is developing rapidly in China. There are more than 50 steel slag cement works which annually produce 3 million tons of steel slag cement with this value continuously increasing.

Slag valorisation by recovery of valuable components. Vanadium-titanium magnetite is smelted by the blast furnace in Panzhihua Steel, China. After smelting, titania is separated from the metal into the molten slag. Based on several case studies in laboratories and in a pilot plant, it has been shown that it is feasible to recovery titania from the slag by a new process: the so-called Selective Precipitation Technique (SPT). This process involves three continuous steps: (1) the selective enrichment of the

dispersed valuable metal compound (VMC) into a designed mineral phase in the molten slag; (2) the selective coarsening of the designed mineral phase with large crystal grain size; (3) the selective separation of the coarse phase from tailing by mineral dressing or hydrometallurgical processes. In case of titania bearing blast furnace slag, titania is enriched in the perovskite phase and separated from other components from the treated slag.²²⁾

The SPT process was also tried for copper smelting slag which contains more than 40% iron, which exists mainly in the forms of fayalite ($2\text{FeO}\cdot\text{SiO}_2$) and magnetite (Fe_3O_4). Experiments were carried out in laboratory scale to study the precipitation and growth of the magnetite crystal from the molten copper slag for the purpose of iron enrichment. The experimental results indicated that the slower cooling rate, oxygen blowing and lime addition into the molten copper slag is favoured for precipitation and growth of Fe_3O_4 . Magnetic dressing is possible to separate magnetite from treated slag after milling.²³⁾

The precipitation behaviour of vanadium phases in vanadium bearing BOF slag was studied.²²⁾ No vanadium enriched phase could be used to separate vanadium bearing mineral from BOF slag when the V_2O_5 content is less than 3%, such as in received BOF slag. Carbothermal reduction can be used to reduce the vanadium-bearing BOF slag to obtain a vanadium enriched phase by adjusting the composition of vanadium-bearing BOF slag. The metal phases are composed of Fe_2SiV , FeSi_4P_4 , and Fe_3C , while the remained slag is composed of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), calcium aluminum oxide ($5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$), and calcium aluminum iron oxide ($\text{Ca}_2(\text{AlFe})\text{O}_5$).²⁴⁾

Conclusions

The hot stage treatment processes for BF slag and BOF slag in China were reviewed. INBA and TYNA processes are becoming popular for large scale BFs. For BOF slag treatment, pyrolytic self-slaking, HK, and BSSF processes are being accepted. However, until now there is no process that can recover heat energy from molten slag in China. The heat recovery from molten slag should be considered for molten slag granulation processes. Large scale application of stabilised steel slag powder in construction is most important. It is hoped that the processing ability of steel slag fine powder will rapidly increase. To be more successful, we believe the research and development activities of metallurgy and cement experts should be better aligned.

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Process Development of Solid By-products from Steel Industry with High Added Value

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Abstract

For the problem of steel slag disposal and steel slag complex utilisation, a modification treatment of steel slag is an efficient method to improve the utilisation ratio of steel slag. The effect and the mechanism of actions to improve the application performance through high temperature ingredient modification were researched. With the new in-process modification technology, the problems of instability, grindability and activity can be effectively solved. Exploration of this technology can promote the bulk application of steel slag and exploitation of high-grade steel slag. Meanwhile, new technology concerning the production of steel slag based ceramics is introduced, and pilot scale plant experiments show that steel slag based ceramics are qualified for use and especially have excellent performance in strength.

Background

At present, the steel production in China is more than 0.4 billion tons per year, and accordingly, the steel slag production represents 50 million tons, only 10% of which can be effectively treated and turned into useful resources. In China, many steel works are focusing on the study of the application of the solid by-products, based on the new concept that the steel slag should never be regarded as a waste, but rather as a resource which should be in cyclic utilisation. Different from the traditional modification procedures for steel slag, which involve processing after the slag is cooled and solidified, in-process modification will reform the steel slag when the slag is still in the liquid state, at high temperature. This process is a laconic and effective treatment and thus makes it possible for the design of advanced materials. In this paper, some research on in-process modification of steel slag was carried out and the development of a kind of steel slag based ceramic was conducted.

In China, technology which turns steel slag into resources has been developed and steel slag has, therefore, found wide use. However, there remains a gap between China and western countries in this field. There are still some problems in the wider application of steel slag, such as low efficiency in magnetic separation, low grindability, low activity

and poor stability. In this respect, development of new technologies to improve the performance of steel slag and make good use of it become significant.

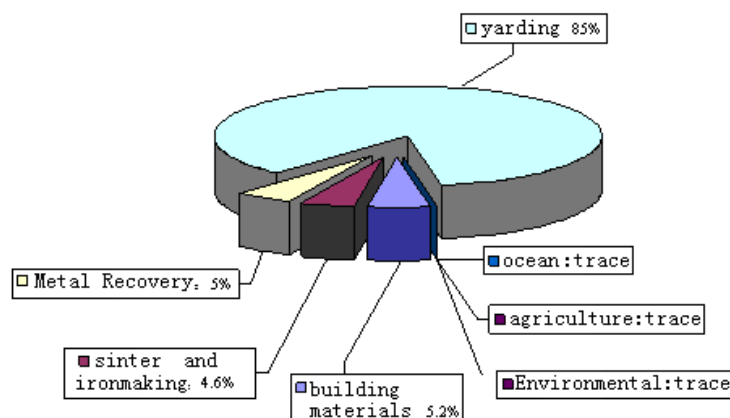


Figure 1: Current application of steel slag in China

The current processes to improve the steel slag properties, such as grinding aid, hot disintegration, are called “after treatment technology”. However, this kind of technology cannot improve steel slag for wider use. Thus, “in-process” technology, which is aimed to solve above problems, is raised in this paper. This technology refers to adding special modifiers into molten steel slag to improve its grindability and stability, and to finally obtain qualitative slag products. In this process, the sensible heat in the molten slag will allow the slag to keep a high temperature and its liquid state, which is a necessary condition for the in-process treatment.

Grindability improvement of steel slag by high temperature in-process modification

In-process modification experiment by adding fly ash to molten steel slag

Fly ash is a kind of anthropogenic ashy active material, generally regarded as “solid waste”. The main constituents of fly ash are SiO_2 and Al_2O_3 oxides, while it also contains some unburnt fine granular carbon. The experimental procedure is as follows: first, some steel slag blocks were melted in molybdenum silicide bar furnace and during this liquid state some fly ash was added. The added amount ranged from 0-30% of the steel slag amount. After sound agitation, the slag was cooled to the normal temperature. Secondly, after primary smashing, the blocked slag was ground in a compact globe mill. Under the same grinding time and conditions, the size distributions of the ground slag powder, to which varying ratios of fly ash were added, are shown in Fig. 2.

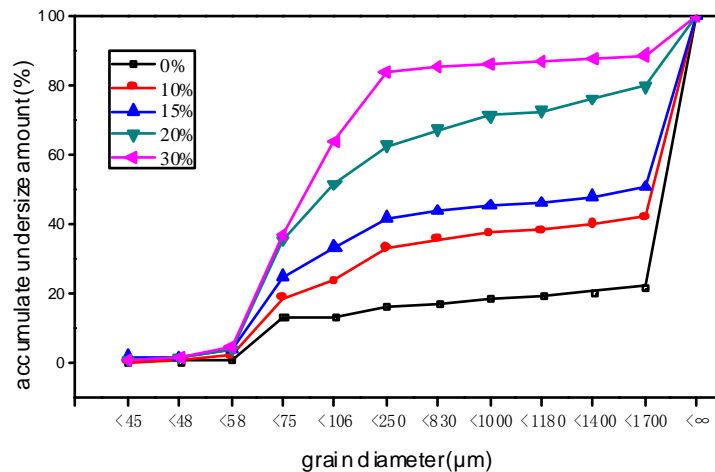


Figure 2: Grain size distribution of different steel slag samples

The experimental results shown in Fig. 2 indicate that, under the same grinding conditions, the percentage of fine particles ($< 75 \mu\text{m}$) in the total slag powder increases from 13.3% in steel slag without any fly ash to 36.9% in the slag with 30% fly ash. For the middle-sized particles (75-250 μm) the percentage reaches 83.81% when fly ash was added. In the reference case (without any addition of fly ash) the percentage is only 16.03%. With an increasing level of added fly ash into the steel slag, the more fine powder can be found in the granular slag. This indicates that fly ash can improve the grindability of steel slag and, with the increasing amounts of fly ash, the grindability of the slag can be sharply improved.

Analysis of XRD and mineralogy

Mineralogical changes before and after steel slag modification process were analysed by XRD analysis. The results shown in Fig. 3 indicate that when the addition level of fly ash reaches 30%, the mineralogical composition becomes simple, with C_2S and C_3S as the main phases, and other phase levels decreasing remarkably. In other words, the characteristic diffraction maximum of ferrous phase like $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ and $\text{Ca}_2\text{Fe}_2\text{O}_5$ and other metal oxide (RO) phases gradually diminish. In fact, with decreasing in free CaO , the slag becomes more conductive, therefore increasing the magnetic separation efficiency of the slag.

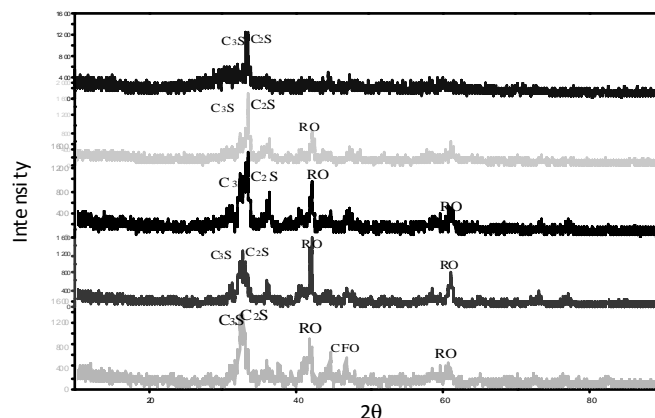


Figure 3: XRD spectra of steel slag with 0%, 10%, 15%, 20%, 30% fly ash

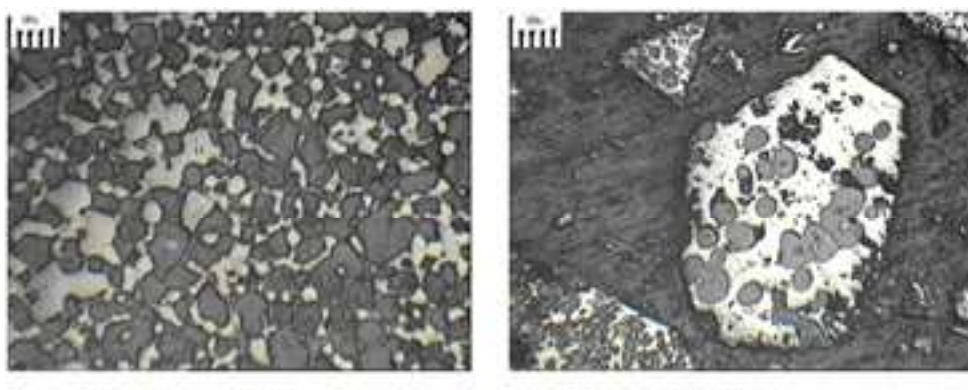


Figure 4: Micrograph of Steel slag with no addition of fly ash: (10, dark grey) = C_2S ; (11) = RO; (15,16) = free CaO

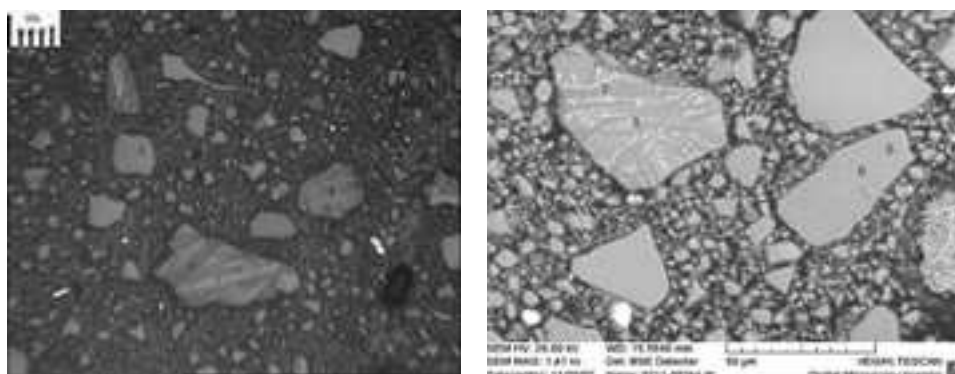


Figure 5: Micrographs of Steel slag with 5% fly ash: (1,2,3,4) = $CaSiO_2$; (5,7) = $CaSiO_2$; (6) = $CaO.FeO.SiO_2$, (8) = RO phase

In order to further analyse the mineralogy and the tectology, slag samples were investigated by polarisation microscope and SEM. The samples were embedded in epoxy resin and polished to thin sections. Mineral compositions were identified through SEM-EDS.

As shown in Fig. 4 and Fig. 5, for the fly ash added samples, new phases like $\text{CaO} \cdot \text{SiO}_2$ and C_2S , some ferriferous oxide and olivine, and more metallic iron were found. Importantly, free calcium oxide decreased dramatically. This kind of mineralogy promotes the grindability. The metallic iron in the slag would increase the efficiency of magnetic separation and thus increase the recycling of iron from the slag.

Close relations between phase changes in the treated slag and fly ash composition are noticeable. The free CaO and MgO in the slag react with SiO_2 and Al_2O_3 in the fly ash, resulting in a decrease of the free CaO in the slag, therefore improving the slag stability. The carbon in the fly ash can serve as a reducing agent to turn weak-magnetic iron oxide in the slag into magnetic iron protoxide or metallic iron, which will help the recycling of iron by increasing the magnetic separation. In addition, the adding of fly ash will promote the emergence of grinding-susceptible phases and the formation of a glass phase with potential activity.

Development of new technology on the production of steel slag based ceramics

The composition of stainless steel slag mainly includes various oxides, and it can serve as a raw material for the production of high value added ceramics. The experimental results show that the principal crystalline phase is diopside, which is the main contribution to the making of high strength and high density ceramics in relatively low temperature. The analysis of the microstructure of the samples indicated that the properties of the ceramics have a close relationship with the firing temperature and time control.

The determination of exact batch formulation is the first step to produce slag based ceramics. In this research, the composition of stainless steel slag was compared with that of ceramic paste. And then according to the result of the comparison, the powder of the steel slag was mixed with certain chemically pure materials, in order to prepare standard ceramic formulations. The next important research is the determination of the firing temperature schedule. In this part, differential thermal analysis of ceramic formula material was conducted and a DTA curve was obtained, which is the key data for the determination of the firing temperature schedule.

Experimental results show that if the ceramics paste includes 30% of stainless steel slag and other necessary chemical materials, the properties of the ceramic samples, such as water absorption, apparent porosity and acid resistance, can meet the demand of general ceramics.

A pilot scale plant test was performed to produce stainless steel slag based ceramics. In this test, 45% of the stainless steel slag was in the ceramic paste and low-temperature sintering was tried, and high strength structural ceramics were obtained. The test results show that all the properties of the ceramic samples conform to national standards. The comparison of the experimental results and the pilot plant scale test results (Fig. 7) shows that more gas pores can be found for the pilot test sample with respect to the experimental sample. This is because the sintering time was too short (55 min) to guarantee full crystalline phase transformation, causing crystal undergrowth. This indicates that there is still potential for the further strength improvement of the ceramics.



Figure 6: Ceramic sample from pilot plant scale test

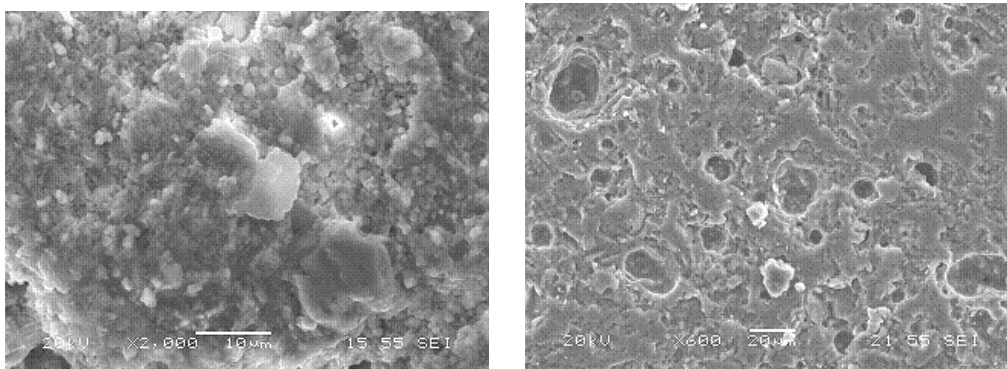


Figure 7: SEM images of the experimental sample (left) and the pilot test sample (right)

Conclusions

The following three conclusions can be derived from the present work:

- (1) Adding fly ash to molten steel slag can promote the grindability. The grindability is improved with increasing levels of added fly ash.
- (2) Mineralogical changes before and after the slag modification process were

analysed. It was shown that there are close relations between phase changes in treated slag and fly ash composition. The addition of fly ash will promote the emergence of grinding-susceptible phases and the formation of a glass phase with potential activity.

- (3) Stainless steel slag can serve as raw material for the production of high added value ceramics. The experimental results show that the principal crystalline phase is diopside, which is the main contributor to making high strength and high density ceramics.

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Overview of Residue Utilisation in Sweden: Focus on By-products from the Iron and Steel Industry

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Abstract

The production of by-products in the Swedish iron and steel industry is approximately 2 million tonnes per year, where the slags stand for approximately 75%. One major issue in Sweden regarding these by-products is whether these materials are waste or products. Even if most of these by-products have been considered as waste, some of them have been sold and used externally, mainly as construction material. But still there are a lot of by-products disposed as waste that could be seen and used as products. In Sweden there is a lot of work going on in this field in order to show, and get an acceptance for, that many of these by-products are a raw material source that can be used in an environmentally friendly way.

Background

The iron and steel industry produce much more than just iron and steel. The iron and steel are of course the primary products, but parallel to these products there are also other secondary products and materials produced at the same time. Some of these secondary materials are today considered as products (or by-products) and others are considered as waste. In Sweden the volume of these secondary products are approximately 2 millions tonnes. As a thumb rule today, approximately one third of these secondary materials are sold as products, one third is used internally and one third is discarded. To this could also be added the iron and steel scrap that also come out as by-products in the different processes. These materials are normally not calculated as secondary materials and almost 100% of the iron and steel scrap is reused and remelted within the steel industry. This material will not be further considered in this paper.

Normally when working with by-products we have the following priorities (not always in this order):

- Decrease or prevent the appearance of the by-products;
- Internal reuse;
- External usage (need of commercial handling, quality demands and environmental issues);
- Disposition (according to the regulations of today).

The utilisation of residue materials from the iron and steel production has a long history and is not a new issue. Already in the beginning of the iron and steel production, many hundreds years ago, the iron producers took care of especially the slags. Even if the priority over the years has gone up and down, it has always been an important thing to keep the eyes on. Today this is considered as a very important objective and the priority has been enhanced.

The figures in the following text are, if not mentioned in another way, based on an internal evaluation within the Swedish Iron and Steel Association that started in 2008 and will be published sometime this year (2009).¹⁾ All these figures should, therefore, be seen as estimations. Nevertheless, they will be close to the final results from the evaluation.

By-products – waste or products?

The definition of waste and by-products and the differences is very important in order to ensure both the usage of the secondary products, and a good and healthy environment. In many cases the interpretation is not a problem. But when coming to secondary products from different industries and maybe especially from heavy industries with high volume of secondary products, the interpretation can be difficult. In Sweden, the authorities normally have considered many of the secondary products from the iron and steel industry as waste (slag, mill scale, dust *etc.*). This has been a general problem when trying to develop applications and usage of the secondary products. Since this is a general problem within the European Union, the Commission has come with tools that help regarding the interpretation of waste and by-products.

The general conclusions of the interpretation are as follows: to ensure that the secondary material (or production residue as it is named in the interpretation) is a product, the material should have a defined usage, should be ready for usage and it should be produced as an integral part of the production process (*see also paper by H. Kobesen in these Proceedings*). Another important part is of course that there should also be a market for the material.

But even if the producer of a by-product considers the material as a product, the authorities might still consider the materials as being a waste. This will in some cases lead to very long discussions and negotiations. As mentioned above, the authorities in Sweden consider a lot of the by-products as waste. This is also the fact regarding by-products that in other countries are seen as products, raw materials *etc.*, *e.g.* slag for construction purposes. The Swedish Iron and Steel Association, among other Swedish branch organisations, are, therefore, spending a lot of time lobbying for a change in the view of by-products and waste. The objective is to get an acceptance for interpreting

many of the by-products as products, raw materials *etc.* instead of waste. For all the by-products we also consider the need of registration in REACH. More information about that is shown below.

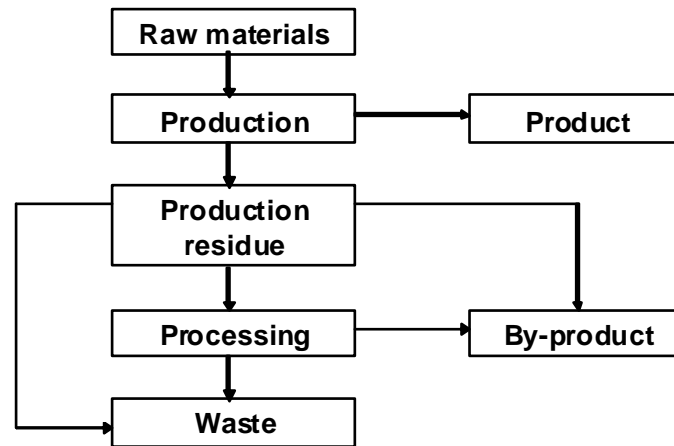


Figure 1: Production chart for products, by-products and waste

Production and usage of by-products from Swedish iron and steel industry today

Production of by-products

The Swedish iron and steel industry produce approximately 1.5 million tonnes of different slags. The absolute major part of these comes from the blast furnaces and the following processes such as BOF *etc.* In total these slags represent about 70% of all the produced slags in Sweden. How all these slags are distributed is shown in the figure below.

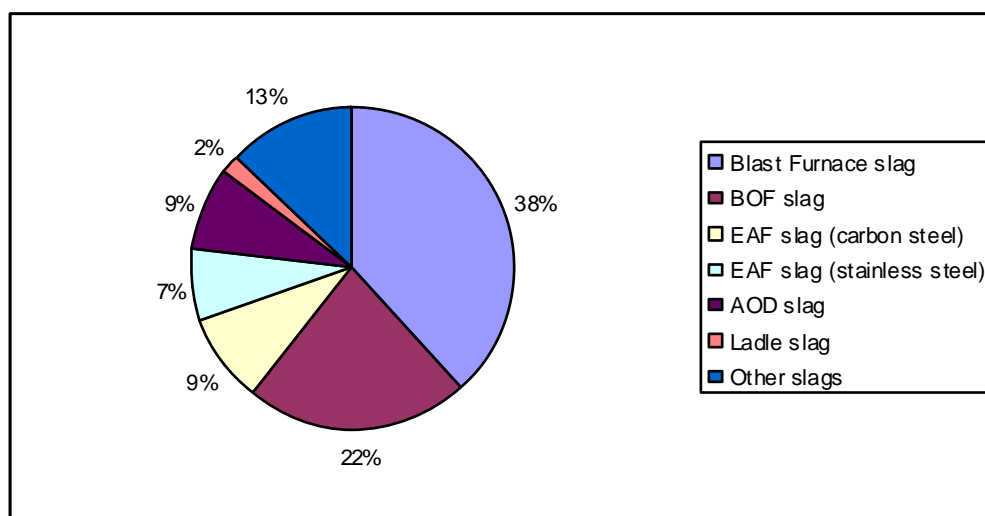


Figure 2: Slags from Swedish iron and steel industry (2007)

Even if the slags stands for the major part of the by-products, there are of course a lot of other materials coming out of the iron and steel processes. In Sweden there is approximately 300 kton of these other by-products. Beside these by-products there are a lot of smaller groups of by-products. Some of them are regarded as waste, others as by-products. This depends very much on possible markets and if the by-products are harmful or not. Normally, very little effort is spent on these materials.

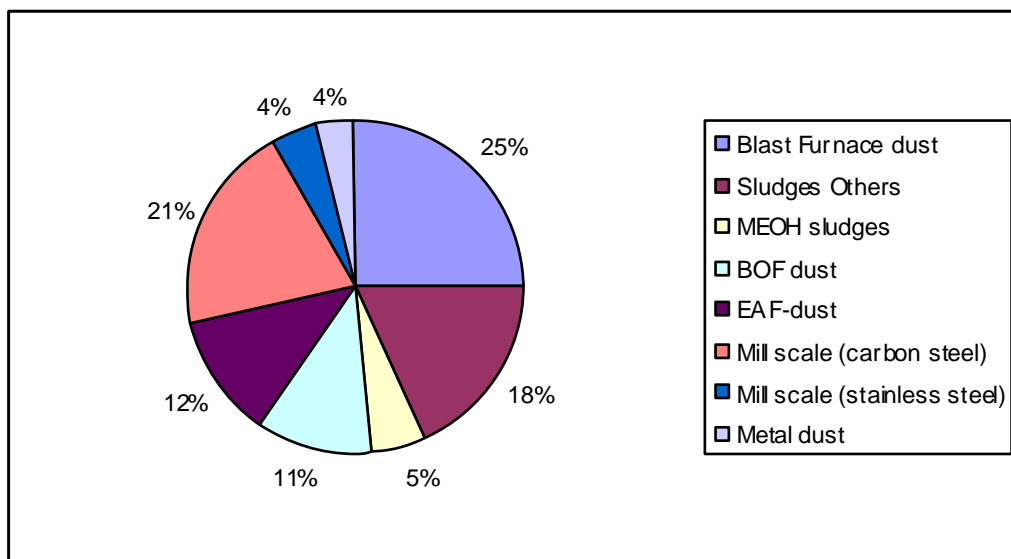


Figure 3: Other by-products from the Swedish iron and steel industry 2007

Usage of by-products in Sweden

In Sweden there has been a change in the usage of the by-products, and specially the slags, over the years, but still there is a lot of slag disposed. When looking at the figures below, it is important to understand that all the slag used as slag former is BOF slag that is internally recirculated within the blast furnace plants. Another thing is that some of the slags used for construction purposes are also used internally within the iron and steel plants and that some of the slags are used when constructing disposal areas. In the latter it can be difficult to define if the material should be considered as a construction material or waste that is disposed. Some of the slags would probably not be able to be used for *e.g.* road construction, due to high concentrations of harmful substances or high leaching levels of these elements *etc.*

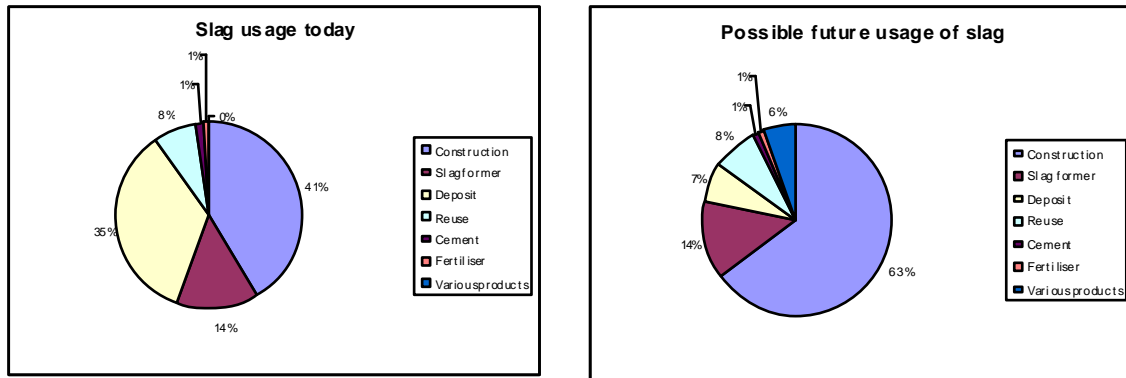


Figure 4: The usage of Swedish slags today and possible usage in the future

The slags that are today used as construction material come mainly from the blast furnaces and the BOF processes. Most of the slag from EAF processes (both carbon steel and high alloy production) and AOD processes are, in general, disposed today. But there is a lot of research going on in this area and this situation will probably change in the future, given that most, but not all, will be able to be used for construction purposes.

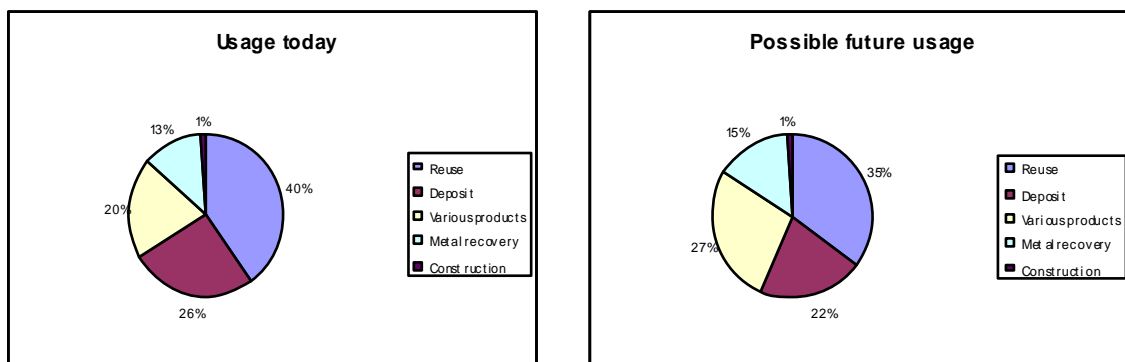


Figure 5: The usage of other by-products from Swedish iron and steel industry

The metal recovery in the figures above comes mainly from the EAF-dust. These dusts contain either high levels of zinc (from the carbon steel production) or high levels of metal alloys (from the high alloy production). There is a significant value in the different metals as well as high costs for disposing these dusts, depending on if they are classified as harmful. Therefore, the recovery of the dusts has been going on for many years in Sweden, and almost all dust is recovered today. The material for reuse comes mainly from different dusts created at the blast furnace plants that go back to the process again.

The future possible usage of the slags (and in some cases for the other by-products) depends a lot on the research and development on the materials that is carried out today. But it also depends on the future regulations in this area and the interpretation of them.

Usage of slags in Europe

There are some significant differences how the slags are used in Sweden compared with the major part of Europe. According to figures from 2006, there is approximately 45 million tonnes of slag produced every year in Europe. A lot of these slags goes to the cement industry. In Sweden this is not the case, or at least very little. This might be slightly changed in Sweden in the future, but probably not in the nearby future. In Sweden we dispose approximately 35% of the slags today, whereas in Europe only about 7% is disposed. This will change in Sweden if we will get an acceptance for a wider use of the slags. We also use a lot of BOF-slag as slag former in the blast furnaces, which does not seem to be the fact in the rest of Europe. But this application might be hidden behind the figures for reuse of various products. When looking at the figures regarding usage of slag for construction purposes, they are quite similar, but the vision is to significantly increase that part in Sweden. This seems also possible since there are a lot of possible applications, especially if the R&D regarding the slags run as planned (more about this below).

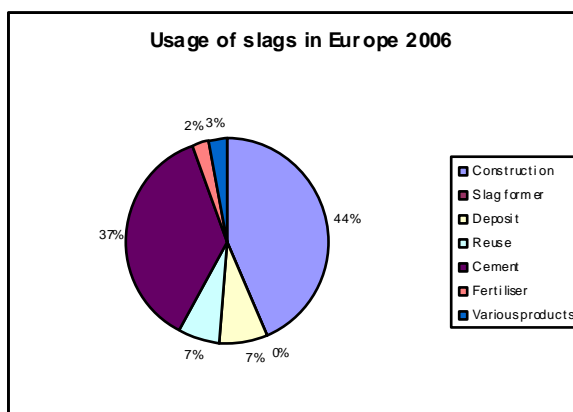


Figure 6: Estimated usage of slags in Europe²⁾

Regulations – Possibilities and Obstacles

In Sweden there are a lot of regulations regarding usage of secondary products. This depends on the general view from the authorities that most of the secondary products are considered as waste. One thing that has been changed the last year, is that the blast furnace slag in some areas and for some applications is not considered as waste. The problem is that not all the Swedish authorities have accepted that yet.

To our help in the future we will have the new harmonising regulations regarding products for building purposes. These regulations will make it possible to use all kind of products as raw material in the building industry irrespective of the origin of the material. But there is of course a need of showing that the material is not harmful *etc.* The material has normally also to be CE-marked.

For materials that today are considered as waste there will be new possibilities. Under the revised Waste Framework Directive there is a project supporting the development of the End of Waste criteria. One of the planned key outcomes of this project is to give a general framework methodology as a guidance to define the end of waste criteria.

The Swedish Environmental Agency (SEA) has suggested a handbook regarding “Guidelines for using waste for construction purposes”. This is something the industry has asked for in order to help both the industry and the local authorities to decide how to use the by-products. But the SEA has in the work with these guidelines decided that the “Non toxic environment” overrules other goals like *e.g.* “Reduced climate impact” and “A good building environment”. As a consequence of that, this has led to very limited guidelines (and possible usage), which focus only on the total contents and the leachability. The proposed guidelines do not really take into consideration the function of the material or the actual quantity used compared to what it replaces. These guidelines are still only a proposal, and the Swedish industry is now working for more usable guidelines.

Another set of regulations that will have an effect on the by-products is REACH (*see also Contribution by H. Motz in these Proceedings*). Since REACH only includes products and not wastes, our interpretation is that if a material is registered in REACH it can not be a waste, at least as long as there is a defined market for the product. Since slags will be registered in REACH, the Swedish iron and steel industry hopes that this will open the door to a wider usage of slags in Sweden as well. The same goes for other by-products such as mill scale *etc.* All materials that are (and will be) considered as waste will be controlled by the waste regulation. In some cases this might still be the best solution, especially if the volume of the by-product is rather low, or if there is a risk (environmental, unstable market *etc.*) involved with the material. To our help we also have the interpretations of differences between waste and by-products mentioned above.

On-going research and development

The research and development in the area of by-products from the iron and steel industry has been carried out since the first iron and steel was produced. But it has been an area with a relatively low focus for a long time in Sweden in the common research. However, during the last years this has changed and today there is a lot of common

research and other activities and projects going on in Sweden regarding the by-products, with the highest focus on slags. One important thing regarding R&D of the by-products is that there is almost no competition in this area. It is then easy to be open about problems, solutions *etc.* in the different common projects. The competition comes instead from other branches.

Most of these projects are in one way or the other run within the Swedish Iron and Steel Association, in cooperation with several companies. The projects include:

- Increased yield of metals from the slags by various methods;
- Stabilisation of slag;
- Slag as construction materials;
- The environmental impact of the slag;
- Eco-loop of slag *etc.*

The institutes involved in these projects are mainly Luleå University and MEFOS, both in Luleå, and the Royal Institute of Technology (KTH) in Stockholm. In total the amount spent on these projects is approximately 9 M€, with a high contribution from the involved companies. To this should also be added all R&D that is carried out regarding slags within the different companies. It is difficult to get a figure for the amount spent on these internal projects, but it is probably also a very high figure. Most of the R&D for other by-products, *e.g.* sludges, dusts, mill scale *etc.*, are also carried out within the respective companies rather than in common projects. This depends on the fact that these materials are very often quite different between the companies or that there is a relatively good solution for the by-products today, requiring a low need of external or common R&D.

The main objective with all these on-going activities is to decrease the disposition of by-products. To reach this, the different projects will show the possible use of the slags, the impact on the environment, the cost benefit by using these by-products instead of other raw materials *etc.* The plan is that all these activities will lead to a changed opinion from the authorities, as well as the rest of the society, regarding the possibilities in, and usage of, by-products.

Process control

As long as there has been a relatively small value in the by-products, there has also been relatively little effort spent on the process control for controlling the by-products. But as soon as the by-products represent a high value this has been changed. The high value can be direct, as a high income when putting the material on the market, or indirect, by avoiding high costs for disposing or recovery by finding an alternative use for the

materials. One good example is the process control when producing blast furnace slags. By an increased process control in the blast furnace it is possible to produce both the iron and steel, and the slag within specifications.

The more the usage of the by-products will be, the higher will be the demand for a process control for the production of these by-products. There will also be demands for other raw materials used in the production of the primary products. This will also have an effect on the R&D for product development as well as for process development. If, for example, new alloying elements are introduced they might have an effect on the slag, the dust, the sludges *etc.* If this is not considered from the beginning this can destroy the whole usage of the by-products.

Future possibilities

By working together in the R&D in the area of by-products, we will be able to find more examples of how to use these products in a cost efficient and environmentally friendly way. Cost efficient means here both for each company but also for the society in general. In Sweden we also have a lot to learn from the rest of Europe regarding the use of by-products in general and especially the slags. The other very important thing for the future is to work more together with the authorities in order to have regulations that are accepted by all parties. If both these things are achieved, there will be a very high possibility for an increased usage of the by-products. This will then give a low demand for disposition, increased income for the companies and a low impact on the environment.

Conclusions

In Sweden the usage of slags and other by-products from the Iron and Steel industry is rather low and different compared to the rest of Europe. This means that much more of the slags are disposed today compared with Europe. The usage is also different. There are a lot of by-products (mainly slags) that in Sweden go towards construction purposes, just as in the rest of Europe. But in Sweden very little of the slags goes to the cement industry. Instead a lot of the slags are used as slag former, which does not seem to be the case in most of Europe.

In Sweden there are very strict regulations regarding the usage of by-products. Usages that are possible and even recommended in other countries are in many cases not allowed or demand a lot of work with permits *etc.* in Sweden. Forthcoming regulations and directives within the European Union will probably change this and increase the usage of by-products in Sweden.

There is a lot of research going on in this field in Sweden. The main focus is to ensure that the by-products will be able to be used as construction materials. A lot of these projects are run as common projects, with many of the Swedish iron and steel companies involved. The Swedish Iron and Steel Association is also very much involved in many of these projects, as well as in the lobbying for these materials.

References

1. Most of the data used in this paper comes from an ongoing work at the Swedish Iron and Steel Association. This will be published later in 2009.
2. Data come from information on Euroslag's website.

Development of an Integrated Evaluation Strategy for the Recycling of Secondary Aggregates

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Abstract

Stony thermal residues such as metallurgical slags and bottom ashes from waste incinerators are valuable substitutes for natural resources. In Flanders, their reuse is regulated by VLAREA. This regulation mainly focuses on the environmental impact. In recent years however, users and customers posed questions about the long term impact of the reuse of slags and ashes. Parallel to the growing awareness, the European Commission launched its strategy on the prevention and recycling of waste. The strategy aims to replace the traditional holistic view on waste management by an approach that focuses on applications and products. This asks for an elaborated evaluation of the physical integrity and environmental impact of the applications and products over their entire life-cycle. In the present article we demonstrate how such an evaluation can be organised.

Introduction

In August 2003, the Flemish parliament voted the decree on surface raw materials [BS 25.08.2003]. The decree defines the framework to come to a rational, sustainable exploitation of surface raw materials such as clay, sand and gravel in Flanders. The legislator recognises that the natural resources are limited. Furthermore, competitive land-use and stringent environmental exploitation requirements limit the access to the natural resources. To guarantee the availability of the necessary resources to future generations, both the exploitation and the use of the valuable natural raw materials have to be optimised. One of the mechanisms to reach this goal is to promote the use of substitutes in applications where it is technically and environmentally feasible. The natural raw materials can then be primarily preserved for high-value application for which substitutes are presently unavailable.

For example, secondary aggregates derived from metallurgical and incinerating processes can serve as substitutes for natural gravel and/or sand. Optimising their reuse in construction works hence will help to meet the goals set by the Flemish government. In 2008, the administration of Land and Soil protection, Subsurface and Natural resources ordered an update of the inventory of the amount of slags and ashes currently generated and reused in Flanders.¹⁾ The inventory indicates that about 2.8 million tons of secondary aggregates are generated annually (Table 1). Slightly less than 2.4 million

tons of these secondary aggregates are currently reused. In total 950.000 tons are directly used as substitutes for surface raw materials exploited in Flanders.

In Flanders, the legal framework for the reuse of secondary aggregates is written out in the Flemish Regulation on waste prevention and management, in short VLAREA.²⁾ The regulation mainly focuses on the environmental quality of the substitutes. In order to qualify for reuse as a secondary raw material, a secondary aggregate has to comply with stringent criteria with respect to the leaching of the heavy metals: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Moreover, the concentrations of specific organic pollutants have to be below certain limit values.

Table 1: Overview of the current reuse of secondary aggregates as substitutes of primary raw materials in Flanders.¹⁾

Slag	Production	Reuse	Clay/loam	Sand	Gravel	Other
	ton/y	ton/y	ton/y	ton/y	ton/y	ton/y
Non-ferrous						
Pb	150.000	76.000			45.000	31.000
Cu	151.000	151.000		80.000	40.000	31.000
FeMo	22.500	17.000			16.750	250
Steel						
LD slag	381.000	380.000		128.000	27.000	225.000
Stainless	330.000	230.000		75.000	155.000	
Others	1.200.800	1.126.300		2.800		1.123.500
MWI						
Bottom ash	210.000	55.000			55.000	
Fly ash						
Power (E)						
Bottom ash	46.000	46.000			46.000	
Fly ash	285.000	285.000	8.000			277.000

The criteria for leaching were derived from an empirical model that estimates the increase of the heavy metal concentrations in the upper 1 m of a soil over a period of 100 years due to a (construction) work in which secondary raw materials are used.³⁾ The model directly relates the impact on the soil to the emission of heavy metals from the work. However, the emissions tell little about the impact of the work on the deeper sub-surface and the groundwater. These impacts can only be assessed by taking into account the chemical interactions and transport behaviour of the heavy metals in the soil. This asks for much more elaborated models.

In recent years the regulator, the industry and the consumers became progressively more aware of the potential risks of the use of secondary aggregates that contain elevated

levels of heavy metals. As a consequence, they started asking for more elaborated evaluation schemes. This trend is clearly reflected in the increased use of geochemical models for the actualisation of existing regulations with respect to waste management and prevention. Also in Flanders, the VLAREA is currently being adapted. Within this context, a risk-based methodology that takes into account the impact on the subsurface and the groundwater is used to define new leaching criteria for secondary raw materials.

At the same time, industry is looking into the effects of the use of secondary aggregates on the long-term quality of their products. Indeed, the slags and ashes can have an impact on the environmental and physical integrity of products in which they are used and their applications. The use of secondary aggregates in construction materials is a relatively recent evolution. Producers and users often do not have the experience, nor the appropriate tools to assess the potential long-term impact. They are, however, well aware of the financial and public consequences of a failing application.

The fear for negative consequences on the long term is not imaginary. In 2004, the reuse of slags and ashes in concrete has been contested due to problems with pop-outs. The cases led to a series of negative articles in local newspapers (*e.g. Het Belang van Limburg* 2.11.2004, *Het Nieuwsblad* 12.05.04). The fact that industrial residues had been used, made people wonder about the risks that these product pose to both human health and the environment. As these questions could not be answered at that time, producers of concrete products became more hesitant to the use slags and ashes. New regulations, adapted measurement protocols and quality criteria may help to build confidence in the use of secondary aggregates as substitutes for natural raw materials.

Waste management and prevention strategy

Since the publication of Communication 666 on 21 December 2005 [COM(2005) 666], the European Commission has been actively pursuing the development of a new thematic strategy on the prevention and recycling of waste. The strategy sets out guidelines for action by the Member States and describes the ways in which European waste management can be improved. The main goal is to reduce the negative impact on the environment that is caused by waste throughout its life-span, from production to disposal, via recycling. This approach means that waste is seen not only as a source of pollution to be reduced, but also as a potential resource to be exploited.

Waste management is big business in the European Union. Since the publication of the first Waste directive [75/442/EEC], the drive to deal with waste in a rational and environmentally sound manner has created various business opportunities. The efforts paid by companies put them ahead of foreign competitors and opened markets all over the world. As a result, the European waste management and recycling industry gradually

rose to an estimated turnover of over 100 billion euros in 2005, creating between 1,2 and 1,5 million jobs. Moreover, the recycling industry is providing increasing amounts of resources to the manufacturing industry. For example at least 50% of the steel and about 40% of the non-ferrous metals produced in the EU in 2005 were derived from recycled materials.⁴⁾

In order to pursue the goals with respect to waste prevention and to further optimise the sustainable reuse of waste resources, the Commission voted a new framework Directive on waste. The basic objective of the new directive is *"to lay down measures with a view to reducing the overall environmental impacts, related to the use of resources, of the generation and management of waste. For the same purposes, it also makes provision whereby the Member States are to take measures, as a matter of priority, for the prevention or reduction of waste production, and its harmfulness and, secondly, for the recovery of waste by means of re-use, recycling and other recovery operations"* [COM(2005)667 Article 1].

The results of the new legislation should be less landfilling, more and better recycling, and more energy and compost production from waste. The framework directive also sets out a procedure to define boundaries for when a waste has been adequately treated and should be considered a product. To determine whether a waste can be reclassified as a secondary product or material, end-of-waste criteria will be defined for specific waste streams and specific applications. Stringent environmental criteria will be set to reduce the environmental risk and health impact of reuse or recycling of waste. In addition, it will also be necessary to set fitness-for-use criteria to ensure that the recycled products can find a viable market. Such fitness-for-use criteria could be derived from existing CEN standards or other similar sources.⁴⁾

The implementation of the new waste directive asks for an integrated, multi-disciplinary approach to evaluate the technical and environmental qualities of candidate secondary products and substances and to set proper end-of-waste criteria. The evaluation will always start from a specific application. It will have to take into account all relevant technical as well as the environmental and health issues (Figure 1). In case the environmental and health requirements associated with the product legislation are not enough to control the risks associated with the secondary product, additional end-of-waste criteria, *e.g.*, limit values for pollutants or limit values for leaching, will have to be defined.

Product quality

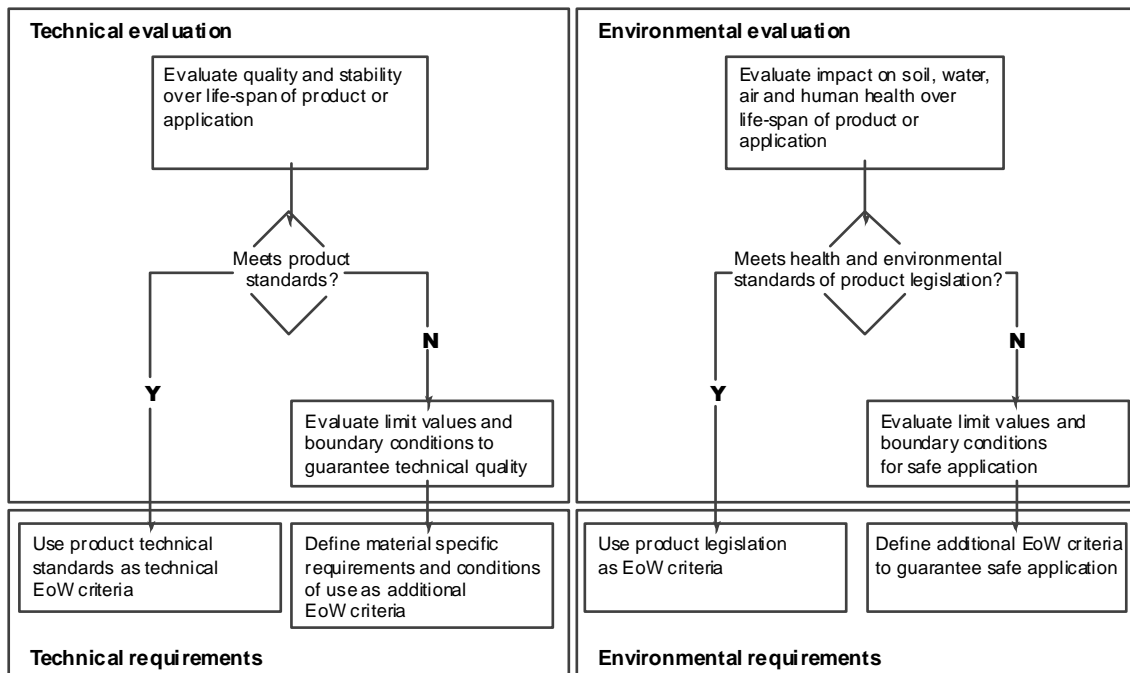


Figure 1: Schematic evaluation chart to set end-of-waste (EoW) criteria

At the moment, specific end-of-waste criteria are being considered for the use of slags and ashes as secondary aggregates. The use of secondary aggregates is not without risk. As discussed below, the properties of the secondary aggregates can have a negative impact on the technical qualities of the end-products or the application. In addition, the chemical properties of the secondary aggregates can also pose risks to human health and the environment. An elaborated evaluation of each of these risks and a proper understanding of the underlying processes is needed to ensure safe reuse of the thermal residues. This will also help to improve their acceptance by users and customers.

In the next three sections, we give a brief overview of how the impact of the reuse of secondary aggregates in construction works and products can be evaluated. We do this by means of three case studies.

Evaluation of the impact on technical properties

A well-known property of several secondary aggregates is their swelling behaviour. In case the swelling is too vigorous, it can negatively affect the physical integrity of the application. One of the most visible examples of damage due to swelling are the so-called “pop-outs” in concrete applications. Pop-outs are holes formed at the surface of concrete due to pressure build-up around an aggregate grain. The underlying mechanism can be physical or chemical. In general, pop-outs are generated by three types of processes:

- Frost damage: Water that penetrates pores within the aggregates can freeze. At freezing, water expands, causing strain in the concrete that can lead to cracks and pop-outs.
- Physical processes: Many of the secondary aggregates have a heterogeneous composition.⁵⁾ They generally consist of a mixture of amorphous, crystalline and metallic phases.⁵⁾ The different phases have specific expansion coefficients. When the expansion coefficients differ too much, large temperature variations will cause strain in the concrete matrix or within the heterogeneous aggregates themselves that can lead to cracks or pop-outs.
- Chemical reactions: Most ashes and slags contain phases that are chemically reactive. Examples are amorphous glass and silica, metals and free lime. These phases are unstable under atmospheric conditions. They dissolve or are gradually transformed into more stable phases, often oxides and hydroxides. In most cases the reactivity of the unstable phases is even further increased by the high alkalinity within the concrete. As a result, the unstable phases will react with cement paste. The interaction can lead to an increase in volume or the formation of new, expansive minerals. Both alkali-silica reactions and the formation of expansive minerals such as ettringite, thaumasite and hydrocalumnite have been described from concrete blocks in which slags and ashes have been used.⁵⁻⁷⁾ Other expansive reactions that can be triggered by the use of slags and ashes in concrete are related to the hydration and carbonation of free lime and magnesium oxide, and to the oxidation of metallic particles⁸⁾.

Standard expansion tests can be used to measure the expansive behaviour of secondary aggregates. These tests, however, do not give information about the underlying mechanisms that cause the expansion. Knowing these mechanisms may help to define the conditions under which the aggregates can be safely used. The type of secondary aggregate and the application will, to a large extent, determine which tests are needed to study the mechanisms that may cause expansion. The choice of the tests will strongly depend on the expansive processes that are likely to occur when a certain type of slag or ash is used (Table 2).

Table 2: Potential causes of pop-outs in concrete made with MWI-bottom ashes.⁵⁾

Process	Risk	Remark	Tests
Frost damage	Moderate	Porous grains	NBN TS 12390-9, petrography
Physical strain	Low	Metallic particles	Swelling, petrography
Free lime & MgO	Low		NBN EN 1744-1, swelling
ASR	Low	Amorphous glass	RILEM TC 106-1, petrography
Ettringite a.o.	High	Related with oxidation of Al	NBN EN 1744-1, petrography
Oxidation of metals	High	Al and to lesser extend Fe and Zn	Chemical (not normalised), petrography

Knowing the mechanisms that may cause expansion is essential to assess the physical integrity of an application over time. Moreover, it can help to define quality criteria for the secondary aggregates and to delineate the conditions under which the concrete products can be used safely. Figure shows images from a petrographical study of MWI bottom ashes used in concrete blocks. The study pointed out that in this case metallic aluminium was the main cause of pop-outs. Oxidation of aluminium sets free Al that interacts with Ca and S from the cement paste to form ettringite and similar hydro-silicate phases. Both the oxidation and the formation of hydro-silicates will result in a volume increase that can cause pop-outs and cracks (Figure 2).

After we identified aluminium as the main cause, tests were set up to study the impact of pop-outs on the compressive strength of the concrete blocks. This test program was defined in such a way that we could also use the results to determine the critical amount of Al in the blocks. As the formation of pop-outs under normal conditions typically takes months to years, VITO developed an aging procedure to accelerate the process. The blocks are partly submerged in water and heated to 80°C at 100% relative humidity. Under these conditions, pop-outs are usually formed within 1 to 2 days.

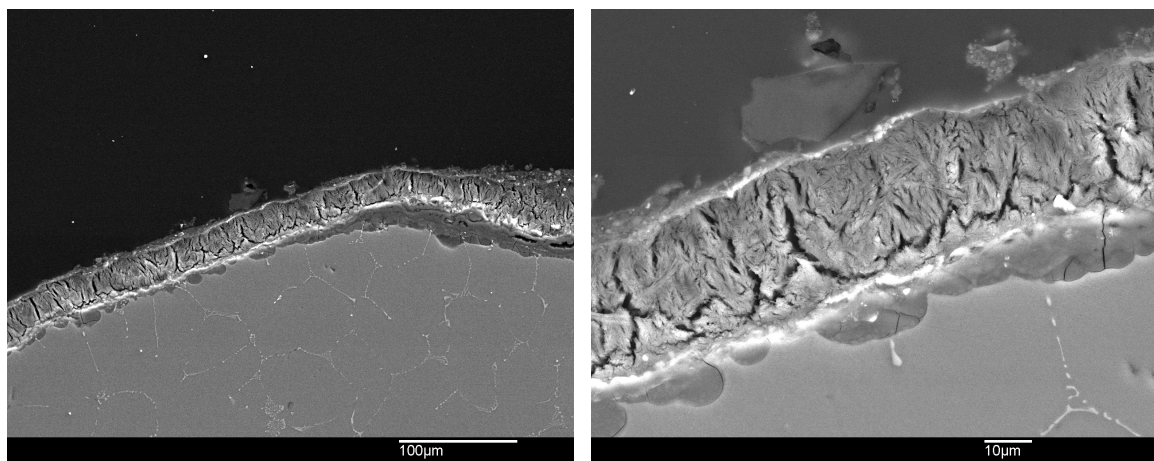


Figure 2: Ettringite formed at the surface of aluminium grain in a MWI bottom ash.

Concrete blocks were prepared that contained different amounts of Al. The blocks were subjected to accelerated aging. The test showed that the critical amount of Al in the bottom ashes varied between 1 and 2.4% depending on the size of the Al-grains. Below the critical Al-content, no pop-outs were observed. Measurements of the compressive strength after 7, 14 and 90 days showed no clear correlation with the amount of Al in the blocks. These observations allowed us to define minimal quality criteria for bottom ashes to be used in this particular application and to develop a procedure to test the quality of the bottom ashes at entrance of the concrete factory.



Figure 3: Cracks formed due to the expansion of elemental aluminium. The expansive reaction was accelerated by partial submersion of the concrete samples in water at a relative humidity of 100% and a temperature of 80°C.

Evaluation of the impact of the environment

Driven by European framework directives on the protection of the soil [2004/35/EC] and groundwater [2006/118/EC], new approaches are being tested to assess the impact of the reuse of industrial stony residues on the various compartments of the environment. These approaches bear on chemical and transport modelling. The last 15 years significant progress has been made in the development of advanced models that allow simulation of chemical processes and transport phenomena in both the application and the soil.

In general we can discriminate between three types of models. The first group are semi-empirical process-based transport models such as *Uitloogmethodiek* (VITO), HYDRUS and PEARL.⁹⁾ The second group consists of geochemical speciation models. Examples of this group are PHREEQC and ORCHESTRA.¹⁰⁾ The third group consists of coupled geochemical and transport models, *i.e.*, HP-1, PHT3D.^{11, 12)}

Models of the first two types are frequently used in regulatory studies, *i.e.* the deduction of new leaching criteria for secondary raw materials in Flanders. In these cases, it is very important to know the limitations of the model used. Contrarily, the third category is better suited to study long-term effects of complex applications. Coupled geochemical and transport models can also be used to assess the impact of an application under varying boundary conditions, *e.g.* changes in redox conditions or changes in the ionic strength of the soil pore water.¹³⁾

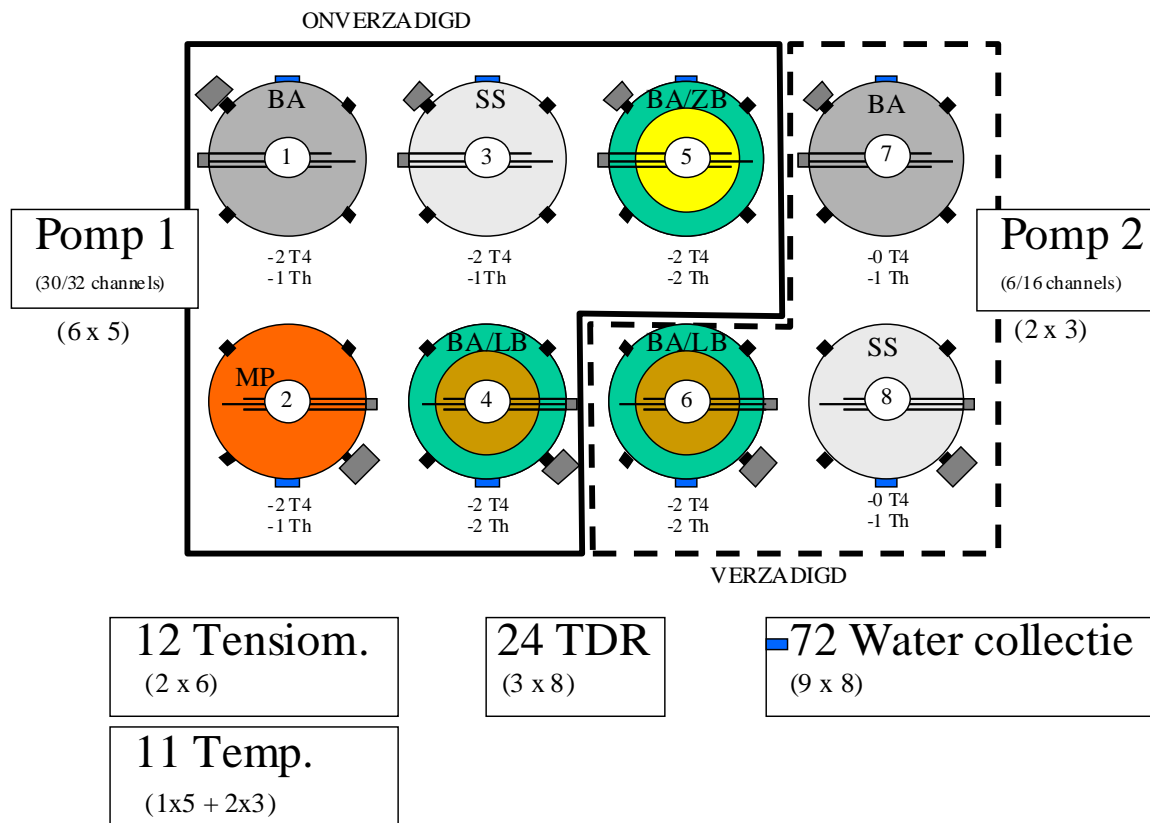


Figure 4: Schematic top view of the lysimeters used by VITO to study the impact of heavy metal leaching from secondary aggregates on soils and ground water. The study is partly funded by the Research Committee of the *Grindfonds* (project OC/GF/08-06).

The European standard EN 12920 defines the methodology that should be used when applying models to assess the long term impact of an application of industrial residues in a work on the long term. An important prerequisite is that the model has to be validated against pilot or field tests. Field tests, however, are complex and expensive to set up. As an alternative, field conditions can be simulated in large lysimeters (Figure 4). Lysimeters allow detailed analyses of the pore water and the soil conditions. They also have the advantage that the boundary conditions can be accurately controlled.

Evaluation of the impact on human health

In 2004, the observation that secondary aggregates were used in concrete raised questions about the health risks of such applications. At that time, objective information about the possible health risk was very limited. There was, and still is, even no clear-cut methodology available to assess this risk. Such a methodology is indispensable to prove that the applications are safe. The Research Committee of the *Grindfonds* therefore launched a project to develop a sound methodology to assess the potential health risks of the use of secondary raw materials as substitutes for gravel in construction works (project OC/GF/07-02).

The potential risk is related to the amount of heavy metals in the applications, the toxicity of the metals present and the way people are exposed to them. The amount of heavy metals in the application varies with the type and the amount of secondary aggregate used. Limit values for exposure to toxic substances are derived from the Belgian regulation for the protection of employees (ARAB) and European regulations on the protection of health, the environment and on qualities of products used in construction.

Table 3: Existing and potential applications of secondary gravel substitutes in construction works (*Grindfonds* project OC/GF/07-02).

Slag	Ready mix concrete	Concrete - roads & infrastr.	Concrete elements & blocks	Asphalt	Unbound applications
Non-ferrous					
Pb-slag	+		- (+*)	-	-
Cu-slag	-	+	+	-	-
FeMo-slag	-	+	+	-	-
Steel					
LD slag	-	+	+	-	+
stainless	-	+	+	+	-
MWI bottom ashes	-	+	+	-	+
E bottom ashes	-	+	+	-	-

*possible but of secondary importance

An essential element in assessing the health risk is the way people can become exposed to the toxic elements present in the application. For this purpose it is important to identify the possible exposure routes. This must be done for each application individually. The starting point for this exercise is a matrix that summarises all existing and potential applications of secondary gravel substitutes in construction works (Table 3). In the next step, the life-cycle of the application is examined in order to identify all processes that could lead to exposure of humans to heavy metals. Within this context it is essential to know how the heavy metals can be set free and how they can become dispersed over the different environmental compartments.

Exposure of humans to the dispersed heavy metals can be direct or indirect. Examples of direct exposure are inhalation of fine dust particles from the air, drinking of contaminated water and swallowing of soil particles. Indirect exposure can occur in case the heavy metals enter the food chain. From a toxicological point of view, it is also important to discriminate between the ways of exposure. The health risks of inhaling or swallowing dust particles is not the same. Indeed, the particles enter the body in a different way and consequently will affect other organs.

To identify all possible exposure routes, each application is described in detail. The first step is to describe all processes that, over the life-span of the application, can lead to exposure. In the next step, the conditions under which the processes take place are defined. This includes a full inventory of the working conditions, the time of exposure and the risk mitigation measures that are or can be taken. Finally the persons that are exposed during each of the process are identified.

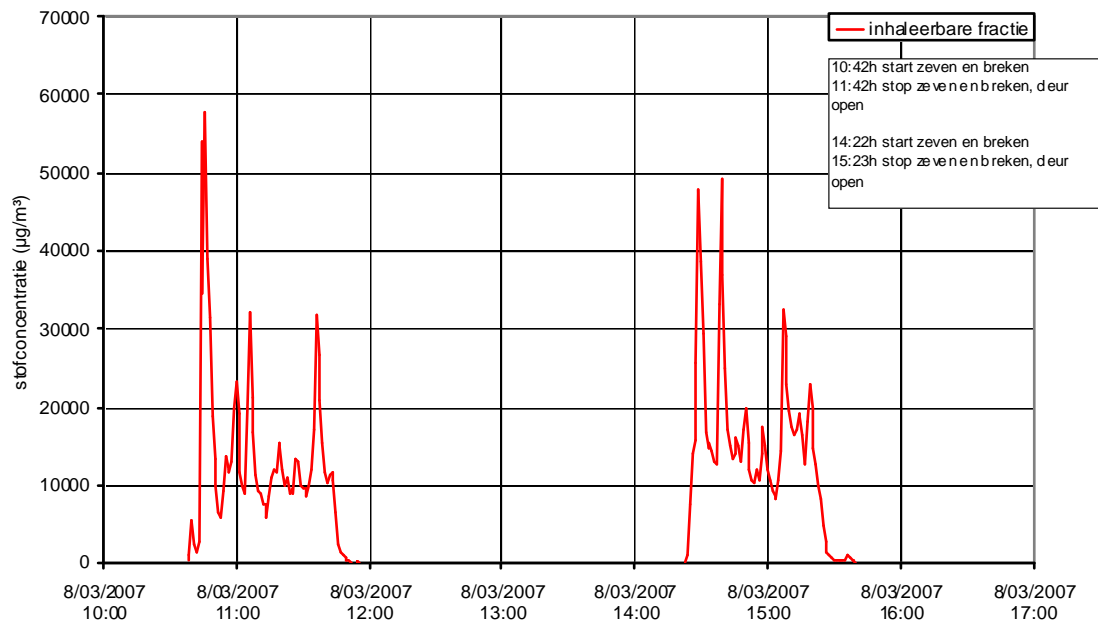


Figure 5: Example of dust measurements of a worst-case exposure scenario during the sawing of concrete blocks in a test chamber.

The exposure routes are then used to set up a sampling and modelling program. To run the models, select measurements of the magnitude of the exposure must be performed (Figure 5). The experiments can be done in test rooms or in situ. Test rooms are suited to simulate simple processes, to create worst-case scenarios or to conduct measurements that are for practical reasons difficult to perform. *In situ* measurements are necessary in case of complex processes that can lead to various exposure routes or that affect several groups of persons in a different way.

Conclusions

In Flanders about 2.8 million tons of secondary aggregates are produced each year. About 2.4 million tons of these secondary aggregates are being reused. In total, 950.000 tons are directly used as a substitute for gravel, sand, loam or clay.

In Flanders, the reuse of secondary aggregates as a substitute for sand and gravel in construction works or building products is regulated by VLAREA. This regulation mainly

focuses on the environmental quality of the substitutes. However, due to negative experience with a few applications, users of the secondary aggregates as well as their customers have posed questions about the long-term effects and health risks associated with the use of these industrial residues.

Parallel with the growing awareness of users and customers, the European Commission pursues a thematic program to improve its waste management policy. The thematic strategy on the prevention and recycling of waste was launched in 2005. It aims at replacing the traditional holistic view on waste management by an approach that focuses on individual applications and products. This asks for an elaborated evaluation of the physical integrity and the environmental impact of the applications and products over their entire life-cycle.

The implementation of the new waste policy asks for an integrated, multi-disciplinary approach to evaluate the technical and environmental qualities of candidate secondary products and substances and to set proper end-of-waste criteria. An evaluation will always start from a specific application, and will have to take into account all relevant technical as well as the environmental and human health issues. A variety of measurements, tests and models will have to be combined in order to evaluate the long-term impact of the application or product on human health and environment, and to define its long-term technical integrity. As is shown by the cases discussed above, the tests can also be used to set adequate criteria for reuse.

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Non-ferrous Slag Valorisation at Umicore: an Overview and a Visionary Outlook

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Abstract

In today's world, the awareness towards the environmental effects of industrial operations has grown tremendously. In Umicore's Precious Metals Refining facility, located in Hoboken, Belgium, 300.000 tons of a complex precious metals feed are processed annually to recover 17 different metals. Although the main purpose of our activities is the valorisation of the feed in terms of precious metals, the complexity of the feed gives rise to different outputs. These can be classified as precious metals, base metals, chemicals and slags. The slag is a FeO-CaO-SiO₂ slag, produced at the lead blast furnace. Due to the complexity of the feed, a lot of trace elements are collected in this slag. Since this slag is used as an aggregate for concrete applications, continuous care has to be taken regarding its environmental behaviour. Our slags fulfill all necessary legal requirements including environmental, applications and ISO certificates to be used in concrete applications.

Next to that, Umicore has committed itself to a sustainable development strategy, aiming to make its economic, environmental and social objectives coherent. This strategy was translated in a sustainable development agreement, signed in 2007, explicitly stating that continuous improvements should be sought to improve Umicore's environmental performance. As a consequence, a roadmap was developed which enables us to valorise our slags in an environmentally friendly way. Apart from supporting the current slag application as concrete, new routes are explored. These include the minimisation of the amount of produced slags, enhancing the stability of the produced slags to lower the metal losses and increasing the metal recovery efficiency from slags, recovering heat from the produced slags, developing new metallurgical processes to reduce the metal losses, aligning the process operations with our "closing the loop" philosophy and continuously search for new applications. From a political point of view, we try to put slag valorisation on the funding agenda of different agencies, for example through joint programs.

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In 2000 slag producers and processors in Europe have come together to form EUROSLAG, the association of organisations and companies concerned with all aspects of the manufacture and utilisation of slag products.

EUROSLAG

Seeks to

- Promote and develop the utilisation of slag in all appropriate situations;
- Ensure slag products are made by the best possible processes using suitable quality control testing and inspection procedures giving the highest level of consistency of performance;
- Provide and encourage communication between slag producers and processors in different countries such that technical advances can be more readily understood and adopted by the whole of Europe;
- Co-ordinate technical working parties and research and development into slag processing and use;
- Bring together people from both the supply and utilisation side of the industry to foster a greater understanding of slag and its benefits;
- Provide a co-ordinated approach to European Standardisation.

The bodies eligible for EUROSLAG membership are

- National organisations, which are representatives of the producers and/or processors of slag from the iron and steelmaking industry in their country;
- Individual companies significantly involved in production, processing, marketing and/or selling of slags, as far as they are not represented by national organisations;
- Associated members.



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