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BLAST-FURNACE AND STEELMAKING SLAGS: WHICH FUTURE VALORISATION IN THE NEXT 20 YEARS?

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Abstract

The major trends and drivers which can affect the uses of slags in the next 20 years are economical and regulatory. The economical drivers are the most important ones: the rising value of energy and raw materials, and the relative market decline, such as cement in some countries, or growth, such as insulation and water treatment. Regulations will generally promote the use of secondary raw materials and the reduction of the carbon footprint in construction. Taking a fresh look at the physical and chemical properties of slags, this should lead to the development of new markets and applications for steel slags and blast furnace slags as well, some of them quite different from the current dominant uses. Of course, it will take years and efforts, associating all players of the value chain, from the steel industry to the end users.

Introduction

Each of us knows that prospective is a difficult and hazardous skill. It is indeed a bold exercise to try to imagine and to draw the future of slags valorisation in 20 to 30 years, while the past shows us that considerable evolutions may take place over the long term, without any sudden change. What can support us in this exercise? We must take into account the drivers, which are the long term trends, economical and regulatory. We must also look with fresh eyes at the physical and chemical properties of the different kinds of slags, in order to perceive how their valorisation could be impacted by the long term trends. It is also useful to examine the worldwide developments in the last few years, which may be sometimes the beginning of great changes. This is how we shall venture to propose some hints, pretending to be neither systematic, nor exhaustive.

Economical and regulatory trends

Slags, as any material or product, are valorised according to market demands, including regulatory constraints. Which are the heavy trends of the next 20 years to be taken into account?

Increasing energy and raw materials value

This considerable economical change, forecast to continue in the long term, has already been the first engine of change in the last 10 years for by-products valorisation in general. Even after the 2008 crisis, prices remain much higher than those known 10 years ago, and the long term outlook is still undisputedly upwards (Figure 1).

This will drive slags producers and users to seek solutions and applications maximising the economical value of the secondary raw materials contained in slags, but also of the contained energy, by substituting slags to products requiring much energy in their production process, such as cement, clinker, lime, or by directly recovering thermal energy. Some uneconomical applications and technologies may so become profitable, opening new fields of valorisation.

A clearer and more rigorous regulatory framework

Regulations became continuously more stringent during the last 20 years in the field of environment protection, in applications as diverse as construction, agriculture, industry, or water management. The environmental impact must be controlled during the whole life of structures, and beyond, by ensuring the end of life recyclability of all materials. This heavy long term trend is very likely to continue. It may restrict the valorisation of by-products, even forbid it, if it imposes environmental constraints which cannot be respected. On the other hand, it may foster and facilitate it if it privileges the use of recycled or secondary materials, while setting up a regulatory framework ensuring a good risk control and allowing progress

Figure 1: Average price of iron ore imported in the UE (15 countries), in €/t[1]

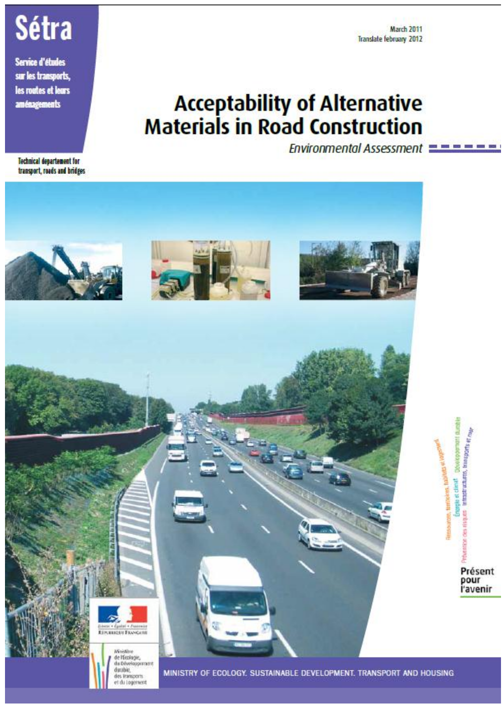

Figure 2: Front cover of the French Guide for environmental acceptability of alternative materials in road construction[2]

and innovation. On the whole, these evolutions are and will be probably favourable to the use of slags. It appears indeed that blast furnace slags and carbon steel slags meet in most cases the imposed environmental limit values, over the world. In the road building field, for instance, the recently published utilisation guides open the path by bringing more clarity to the end users, increasing trust, confidence and professionalism, as a key to allow more and better uses of slags (Figure 2).

The requirements of sustainable construction

The new French regulation RT 2012 (Thermal Regulation 2012) regarding new buildings aims at limiting the energy consumption at 50 KWh/year/m^2, and future regulations being prepared will set the objective to create positive energy buildings. Similar regulations are enforced in the other European countries. Besides, in all production processes of construction materials, recycling is optimised in order to reduce the environmental footprint of the end product. This trend will foster more use of materials having a low CO_2 footprint thanks to their origin. Among them, slags will find a growing demand. Moreover, the new thermal insulation requirements will induce a strong development of the market of insulating materials, such as rock wool or lightweight aggregates for concrete.

A more sustainable agriculture

The brilliant past of the phosphorus rich "scories Thomas" in France, or "Thomas dünger" in Germany is well known. Sustainable agriculture is a deep seated societal movement aiming particularly to save fertilisers produced from oil and non renewable natural raw materials. This trend already encourages and will promote the use of converter slags, bringing lime and oligo-elements, especially in acid soil areas where the lime content of slags takes all its importance. A negative effect may come, on the other hand, from new regulatory constraints restricting the content of some elements, such as chromium.

Growing requirements of water and soil pollution treatment

The regulatory requirements in these fields are undeniably increasing. Thus, the new European regulation for water sets more stringent quality criteria of wastewater discharged into rivers. The same is true for contaminated soils treatment. Seaports and waterways are subject to regulations compelling them to manage in a responsible way their dredging sediments. This particularly implies to stabilise them so as to prevent the leaching of the polluting elements and, if possible, to valorise them. Steel slags, as shown by several experiments around the world, can contribute to the technical solutions developed in this field.

Technical developments achieved in the last 5 years

Aggregates and hydraulic binders have been for years the major markets for slags from the steel industry. Naturally, many developments have been, and are currently carried out in order to increase the market volume of these alternative materials, and/or to increase their market value. However, some developments aim at radically different applications. Here are a few examples.

Developments already at industrial stage

These developments mainly concern steel slags. In the ArcelorMittal Gent plant in Belgium, it is the case of the convertor slag stabilisation process by sand and oxygen injection into the liquid slag, derived from the previous process developed in TKS Duisburg, and adapted to the local conditions (slag chemistry, temperature, market objectives). This installation is now able to produce several tens of thousands of tonnes a year of converter slag ensuring less than 0.1% volume expansion (Figure 3). In the ArcelorMittal Dunkerque plant in France, following a development effort during several years by the companies SGA and Eiffage, based on a converter slag sorting model created by the plant, a road hydraulic binder containing more than

Figure 3: Stand for injection of sand+O_2/N_2 in molten convertor slag in AM Gent[3]

40% converter slag could be successfully marketed. Converter slag is now referenced as possible major constituent of Road Hydraulic Binders in the NF EN 13282 French standard.

China, which produces more than 50% of the world steel production, is active and innovative in the field of slag valorisation. Since more than 15 years, Chinese cement standards allow the use of converter slag up to 20% blended with Portland cement (YB/T022-92 standard).[4] Recent developments also show that in blast furnace slag cements, granulated blast furnace slag can be substituted by converter slag up to 20%.

Developments at pilot stage

This is the case of the use of blast furnace slags in geopolymers. This recent technology, based on still complex chemical activators, enables to produce binders reaching strengths of several tens of MPa at 7 days, using as main constituents (more than 50%) granulated blast furnace slags or fly ashes. These formulations are still subject to difficulties of scale-up from laboratory conditions to industrial conditions, mostly due to local disponibility of resources and no-user friendly activators.[5]

Today, in France and Germany, a European project aiming at using steel slags in filters to extract phosphates from wastewater in small communities equipped with filters planted with reeds, is achieving good results. It will be possible to grind the slag when the filter will need to be replaced and use it as fertiliser (Figure 4).

Figure 4: Filtration basin for the treatment of water from a small town in France[6]

Converter slags also have useful properties to treat contaminated soils. One solution foreseen to stabilise dredging sediments in seaports, or other sewage sludges, would use ground converter slag blended with cement to bind the material and fix the pollutants.[7] This process could even produce artificial aggregates usable in road structures.

Lastly, we need to mention the numerous works carried out in Japan and Korea regarding the application of converter slags to bring iron as oligo-element in sea waters, and life support for marine organisms. Converter slag is immersed in the form of blocks of diverse geometry (BioSlag, Marine Block, Biverly Box), so as to increase the biomass, such as phytoplankton, the slag quantity per cubic meter of water being carefully controlled (Figure 5).

Slags development potential, physico-chemical approach

Examining with fresh eyes the thermal, physical and chemical properties of slags, and the potential resulting values, enables us to step back and to open up the field by

Figure 5: "Bioslag" bloc for sea water oligo-elements enrichment[8]

pointing new avenues and pathways for value development. To better valorise these specific and differentiated properties is the stake, both economical and environmental.

The considerable thermal potential of slags

Slag is tapped from the blast furnace in 100% liquid phase, at 1500°C, and this thermal energy is not recovered, that is roughly 1800 Megajoules per ton of slag, equivalent to the combustion energy of 60 kg of coal. Converter slag is tapped from the reactor at a temperature between 1550 and 1700°C, its thermal content is about the same, and is not recovered at all. The same happens in electric arc furnaces.[9]

The chemical potential of slags

The chemistry of blast furnace slag is optimised for the blast furnace process by setting the CaO, MgO, Al_2O_3 and SiO_2 contents, these last two elements being imposed by the raw materials, and the other two being adjustable (Table 1). These chemical elements are of utmost importance in numerous industries, primarily in construction. The CaO content alone, available in decarbonated form, is worth 30 € per ton of slag. Similarly, the alumina can be worth from 10 to 40 €/t of slag. Besides, CaO-MgO-SiO_2-Al_2O_3 combination not only allows the slag to be perfectly liquid and fluid, easily to control, but also to produce a vitreous material by quenching.

Table 1: Average composition of a blast-furnace slag

Element	CaO	SiO_2	Al_2O_3	MgO	S	Alcalis	TiO_2
%	35-45	35-40	10-15	6-8	0.5-1	0.5-1	0.5-1

The converter slag is designed first of all to eliminate the C, Si, Mn, and P from the hot metal after oxidation, while remaining sufficiently fluid. This fluidity is achieved with the additions of quick lime (Table 2). Finally, the slag must protect the converter refractories, thanks to the additions of dolomite (CaO-MgO). The resulting chemistry is complex, but of high potential value, mainly thanks to the oxidised iron, worth 30 € per ton of slag, and the decarbonated lime, free or combined with silicates, as in portland cement, worth close to 50 € per ton of slag. It is almost impossible to vitrify this slag, due to its high lime content, creating crystalline networks.

Table 2: Average composition of a converter slag (*= after metallics recovery)

Element	CaO total	CaO free	SiO_2	Al_2O_3	MgO	P_2O_5	Fe total *
%	40-60	5-15	10-20	1-3	6-8	0.5-2	10-25

The physical potential of slags

Once cooled down, slags exhibit physical characteristics derived both from their chemistry and the applied treatment and cooling process.

Crystallised blast furnace slags may be regarded as natural aggregates of about 2.2 ton/m^3 bulk density, not subjected to the alkali-granular reaction affecting concrete. Converter slags, because of their higher iron content, are denser (2.4 to 2.6 ton/m^3), and more resistant to abrasion than the usual natural aggregates, but their volume instability due to free lime limits their use to unbound applications.

Slags are tapped in liquid phase out of iron or steel making reactors, potentially allowing much freedom of shaping and modelling, without any melting or sintering. Thus, slags can be granulated or finely sprayed to obtain fine grain sizes, but also fibrillated (in certain viscosity and temperature conditions), moulded in more or less large boxes (Figure 6), or even expanded to produce lightweight aggregates with lower than 1.4 ton/m^3 density.[10]

Thermal and physical characteristics of cold slags are still not well known today. Practically no information is found on the intrinsic values of thermal diffusion, acoustic diffusion, and magnetic susceptibility of slags. Some research is, however, underway in several R&D projects in which ArcelorMittal is taking part.[11] One may, however, consider that blast furnace and steel slags are refractory materials up to 1000°C, and their magnetic susceptibility (for converter slags only, due to its high iron oxide content) appears only in very intense fields (several thousands of Gauss, according to the nature of the iron oxides).

Figure 6: Steel moulds for BOF slag cooling in China Steel Corporation (Taïwan)

Prospective outlook: new treatment processes and new markets

Building on the analysis of the deep economical and regulatory trends on one hand, on the intrinsic characteristics of slags on the other hand, and the R&D works underway, we can try to outline some long term development pathways and areas, without forgetting that, as our experiences show we need ten years to make a new application industrially recognised, and ten years more to make it widespread….

High growth and value potential markets

Some existing applications already take the advantage of specific physical and chemical slags properties, such as heavyweight concretes containing electric arc furnace slags as aggregates, chemical additions for Portland or aluminous cements, as well as air-cooled blast furnace slag for rock wool.[12] The volumes are sometimes limited by some chemical constraints, and there is room for improvements in order to fully develop the use of slags in these growing markets.

Converter slags are an excellent raw material for steel making (iron, decarbonated lime). However, the loop of impurities (phosphorus, manganese) back in the converter creates a strong limitation. ArcelorMittal has developed numerical models taking into account particular technical constraints of a particular steel plant. Some European sites have been able to double their recycling capacity, exceeding 20% of their slag output.[13] This internal valorisation should indeed be the priority not only for plant managers, but also for research and development projects.

Figure 7: Pilot for the spinning disk technology by Siemens-VAI[14]

The capture of the slags latent heat is a priority focus in engineering companies such as Paul Wurth, Siemens-VAI, CSIRO, and Chinese or Japanese steel makers. The proposed technologies recover the heat through air (rotating disc technology, Figure 7), by cooling rolls, or by blending with other solid media. It should be noted that these developments are essentially focussing on blast furnace slag, because of its stable chemical composition, and they allow maintaining or even improving its valorisation in cement.

Breakthrough applications and processes

The real breakthrough is not originally derived from technology, but from focussing efforts towards a new major application field which is a complete break from usual markets.

For converter slags, the point is to consider them fully as raw materials for steel making. Ore processing technologies are then required so as to enrich and purify these slags. This is the goal of the French projects ORLA and LACTER, led by ArcelorMittal in partnership with major public Research Institutes. The objective is to reach a guaranteed internal recycling rate of 50%, while allowing the external valorisation of the remaining fraction (Figure 8).

An indirect way to take advantage of the high temperature of slags is to achieve immediate shaping, whereas other materials require melting or agglomeration of powders. Such is the case for heat exchangers used for heat storage, which is a strategic issue in electricity production from renewable energies. The high cost of usually used materials justifies developments on slags treatment processes, such as cooling and even additions in the molten slag (so called slag making), in order to meet the mechanical and thermal requirements of these applications.[16]

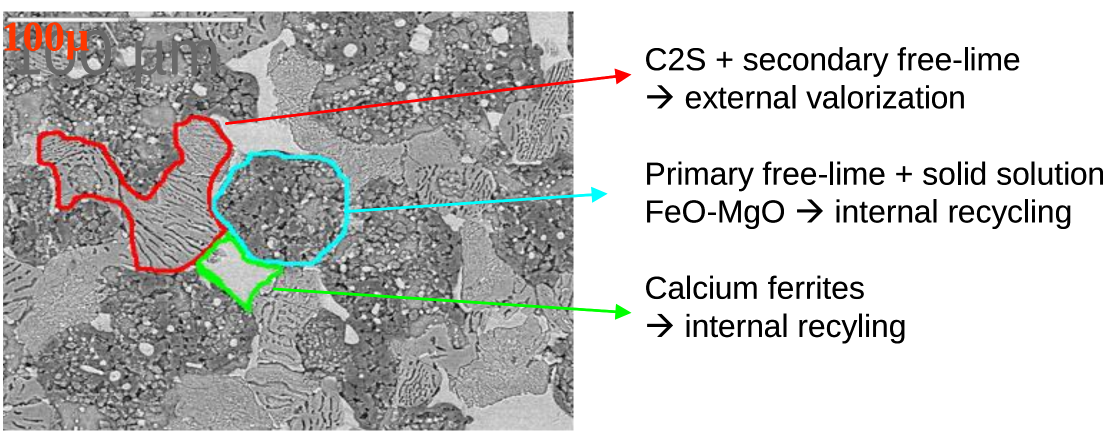

Figure 8: Distribution of converter slag minerals and valorisation interest[15]

Some breakthroughs could also be renaissances, such as the production of expanded blast furnace slags, which could advantageously substitute current materials produced in distant quarries (pumice from Italy, Crete, Iceland,…) or energy consuming processes (expanded clay or shale, sintered ashes). The market segment is booming as a result of growing thermal insulation requirements for buildings. Expanded blast furnace slags were produced 30 years ago in France and other countries,[9] but most of the competencies have been lost, and technical standards and environmental regulations have evolved, which makes new development works necessary in this field.

Another completely new way of valorisation could be to valorise particular trace elements contained in slags, which can become more and more valuable. For instance, certain iron ores may generate significant vanadium content in converter slags, up to 10 kg per ton in some European plants. This is usually seen as a potential environmental risk, but may also be seen as a source of value. Vanadium is sold at around 20 € per kg, and extraction processes and costs, as well as consequences on the valorisation of the remaining slag fractions, should be studied in depth.

Conclusions

There is no doubt that slags have a brilliant future. A new exciting page of their history will be written in the next 20 to 30 years. It will be marked by an orientation towards higher values under the pressure of rising raw materials and energy costs, and regulations, by valorising their specific differentiating chemical and physical properties on different markets. As well as the aggregates market has become secondary for blast furnace slags in the past 30 years, it is possible that steel slags find their value in several other applications. In order to have these developments well focussed, efficient and accelerated until they succeed in the markets, it will be highly necessary to associate in partnership projects the competencies of all the players of the industrial value chain, from the steel maker to the end user. Challenges and roadblocks will have to be overcome, technical, regulatory ones, for sure, but the hardest one might be the difficulty of access to the market.

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