THEMATIC SECTION: SLAG VALORISATION

Granulation and Heat Recovery from Metallurgical Slags

Mansoor Barati[1] · **Sharif Jahanshahi[2]**

Abstract

Metallurgical slags are produced at a massive rate of over 750 Mt/year, and carry a thermal energy equivalent to 40 Mt/year of coal. The potential mineral and thermal energy values of slags are in the order of $22 b and $3–6 b per year. Such attractive figures, together with tightening legislation on disposal of slag and the carbon footprint associated with the loss of mineral and energy values of slags have created a significant thrust in the past decade to develop sustainable approaches for full utilization of slag and its waste heat. As a result of extensive R&D in this area, the slag-processing technologies are slowly converging around dry granulation combined with heat recovery. In this paper, the slag granulation and heat recovery options are reviewed and given a critical evaluation, aiming to provide a basis for future directions in slag handling.

Keywords Slag · Granulation · Heat recovery · Energy

Introduction

The metals industry is under ever-increasing pressures to reduce its energy and resource intensity and environmental footprint. While major strides have been made in this regard by increased recycling of metals, the introduction of breakthrough technologies such as steel continuous casting, or energy recovery from waste gases, few options have remained to further the metals industry towards the zero-emission goal. Metallurgical slags are now generated in excess of 750 million tonnes annually. Slags being discharged at temperatures typically above 1200 °C carry a substantial amount of heat. As expected, the "materials" and "energy" values of the slag pose both a significant environmental liability and a cost, if not utilized. At the same time, they present a major opportunity for the metals industry to become more sustainable by treating the slag as a secondary resource rather than a waste. Driven by this, slag processing technologies are being developed at an unparalleled pace.

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In particular, conversion of slag to value-added products and energy recovery from slag have been of greatest interest, with dry slag granulation evolving as the missing piece of the puzzle that enables both of these. In this article, the recent developments in slag processing and energy recovery are discussed.

Metallurgical Slags: Production Rates and Uses

Production Rates

Table 1 summarizes the slag rates for pyrometallurgical production of various metals, together with their enthalpy values, estimated based on data available for the year 2016. As seen, the production of slag has exceeded 750 million tonnes per year, of which 85% is only from the iron and steel and related industries. While the non-ferrous metal producers are responsible for only 15% of the global slag generation, their significantly higher specific slag rates (slag:metal ratio) results in comparable or even greater slag production to the steel plants in individual operations. For example, an integrated steelmaking operation with an annual capacity of 4 Mt steel would generate approximately 2 Mt of slag, whereas a laterite nickel smelter of only 70,000 t Ni/year could generate over 3 Mt of slag. Consequently, the energy

Table 1 The amount and energy value of metallurgical slags (year 2016) [1–6]

Metal	Slag production (Million tonnes/year)	Enthalpy (GJ/t)	Total heat (Million GJ)
Hot metal (BF)	330.2	1.6	528.3
Crude steel (BOF)[a]	151.1	1.5	226.7
Crude steel (EAF)[a]	70.5	1.8	126.9
Ferroalloy	91	1.6	145.6
Stainless steel	15	1.7	25.5
Ni—Laterite	54	1.6	86.4
Ni–Sulfide	7	1.2	8.4
Copper	34.5	1.2	41.4
Lead	2.74	1.4	3.84
PGM[a]	1.75	1.5	2.62
Zinc	1.3	1.2	1.61
Total	759.1		1197.2

[a]*BOF* basic oxygen furnace, *EAF* electric arc furnace, *PGM* platinum group metals

and material values of the slags need to be considered on a case by case basis.

Energy Content

The thermal energy contained in high temperature slags is substantial and can range from 10 to 90% of the total energy input to the process depending on the specific slag rates. On a global basis, the theoretical heat contained in metallurgical slags is in the order of 1.2×10^9 GJ, equivalent to 40 million tonnes of coal (TCE), 196 million barrels of oil, or 330 TWh of electricity.

Economic Value of Slags

The mineral value of metallurgical slags vary widely based on the chemical and physical properties of the slag as well as regional factors such as availability of natural aggregate, demand for building and construction materials such as cement, etc. In the following table, typical NA prices for various slags are presented as guidelines. The value of slag is expected to increases by the introduction of carbon taxes, as the use of slag is associated with significant reductions in CO_2 footprint compared to equivalent natural minerals, particularly in the cement industry (Table 2).

The net energy contents of various slags were provided in Table 1. These present the maximum amount of heat that can be recovered from the slag. The actual energy harvested is significantly lower because (a) energy losses during the processing (b) due to rapid cooling, the "crystallization" heat of slag is lost, which has been shown in one study [7]

Table 2 The selling price of various slags private inquiries, [4]

Slag type	Price range ($/tonne)	Avg. price ($/tonne)
Ground-granulated BF slag	11–110	60
Air-cooled BF slag	3.5–13.0	7.5
Steel slags (aggregate)	0.5–35	5.5
Copper slag abrasives	150–300	220

to be ~ 17%, and (c) unrecovered energy as it is impractical to transfer the entire enthalpy of slag from its highest temperature to the ambient temperature; the slag discharge temperatures are substantially higher than the ambient. For these reasons, and considering the typical HRE (heat recovery efficiency) values reported in the literature, a reasonable recovery would be 50% (thermal to thermal). With this, and using the weighted average enthalpy of all slags at 1.6 GJ/t, the effective thermal energy recovery from slag is ~ 0.8 GJ/t. The value of this energy can be estimated as follows.

If the slag thermal energy is used directly for heating purposes (e.g. drying), the energy value of 1 tonne of slag is equivalent to 0.13 barrels of oil (6.1 GJ/barrel oil). At current international price of oil ($55/barrel), the value is $7.2/t slag. If natural gas with an average price between Europe and the US is used as the calculation basis, the dollar value is 0.8 (GJ/t) × (5 $/GJ) = $4.0/t of slag.

Alternatively, the estimate can be made by assuming that the recovered heat is converted to electricity. With the conversion efficiency of ~ 35%, and electricity prices of $0.1/kWh, the value is 0.8 (GJ/t) × 0.35 × 277.8 kWh/GJ × 0.1 $/kWh = $7.8/t slag.

Taking the total amount of slag produced from Table 1, and the above rates, the realistic dollar value of slag energy is in the range of 3–6 billion $/year. The materials value of only BF slags, if fully utilized for cement at $60/t, is ~ $20 billion, whereas assuming all other slags are utilized in construction at $5/t, their value is ~ $2 billion/year.

In light of more stringent regulations on emissions particularly on greenhouse gases, the utilization of slag energy could have secondary benefits by a reduction in CO_2 emissions in the same or other industries. For example, if the heat of slag is used to replace oil, the reduction in CO_2 assuming 50% HRE, is 0.8 GJ/t × 0.07 tCO_2/GJ = 0.06 t CO_2 per tonne of slag. For the world production of slag at 760 Mt, this amounts to 43 million tonnes of CO_2, equivalent to removing nearly 24 million vehicles from the roads of Europe, or is valued at ~ $650 million with a carbon tax of $15/t. CO_2. Finally, an even additional reduction in CO_2 is realized from the material value of the slag. For example, it has been estimated that the use of 50% granulated BF slag in a cement mix reduces the CO_2 emissions from 1.2 to 0.54 t/t cement [8].

Fig. 1 Utilization of BF and steel slags in Japan and Europe in 2016 [9, 10] (units in Mt) (color figure online)
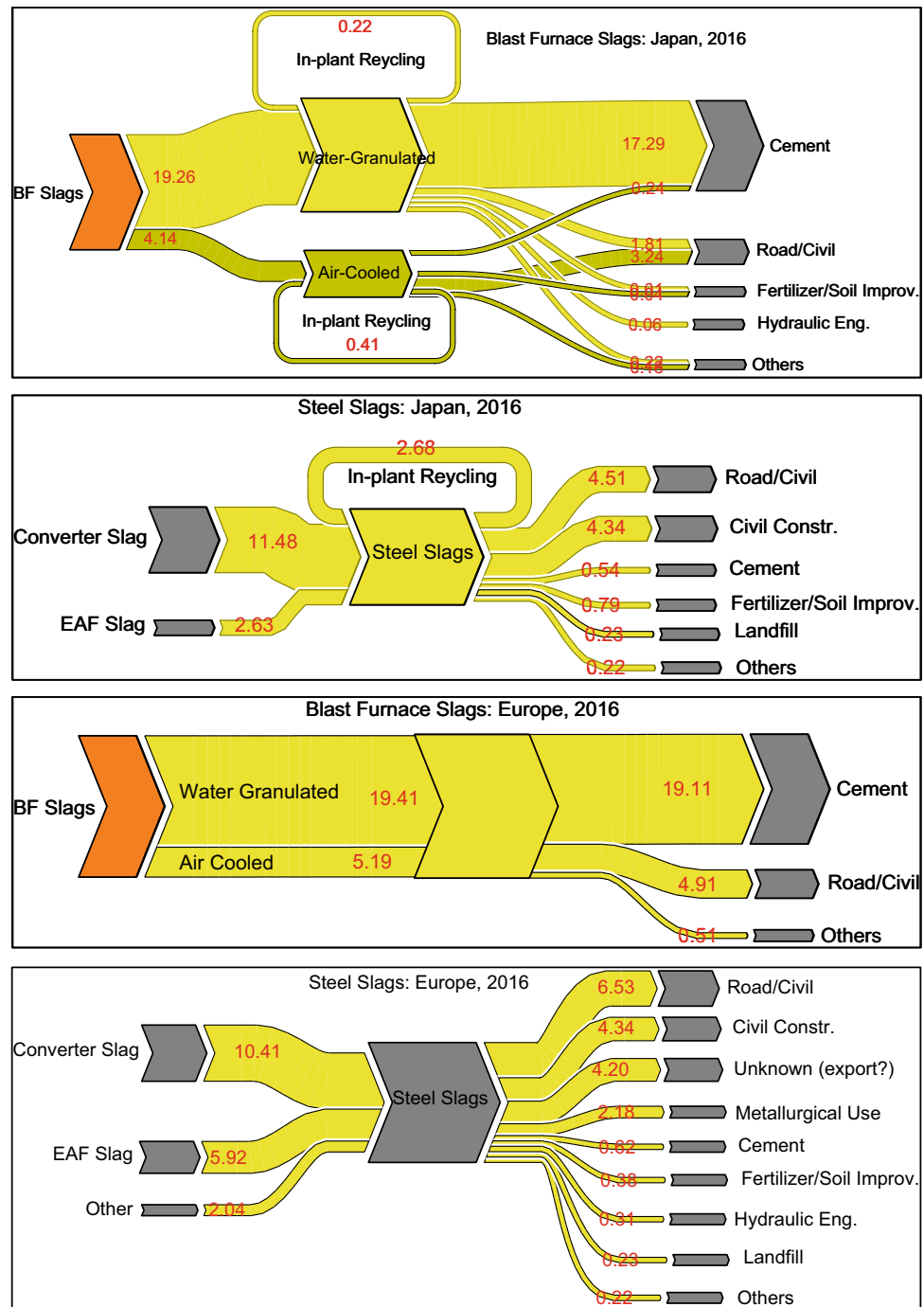
If all the BF slag were directed to cement, this would constitute an approximate reduction in CO_2 of 435 Mt per year, with a value of over \$6 billion in carbon credits.

Utilization of Slags

The slag utilization rates vary widely from one operation to another and appear to be strongly linked to the legislation. There is no information on the global utilization rates, but limited data are available on the fate of slags in Europe and Japan. These may be regarded as the "best practice" of today's slags use and the direction expected to be followed by other countries when the legislations are in place. Figure 1 shows the end use distribution of blast furnace and steel slags in Europe and Japan for the year 2016. As seen, the figures are comparable and show that steel slags are primarily used in road building and construction, as aggregate. The use of the BF slags depends on their cooling methods, those granulated by water are used in cement making whereas the air-cooled slags find uses similar to steel

slags. A small portion of non-ferrous slags (e.g. copper) is converted to abrasive materials or grinding media in mills, the majority are stored in slag yards or landfilled.

Processing of Metallurgical Slags

Conventionally, little chemical adjustments are made to the slag prior to its processing for subsequent use or disposal. However, recent attempts have looked into modifying the chemical composition of slag while hot, to render its chemistry and properties suitable for high-value products or recovery of minerals/metals from slag [11, 12]. Nonetheless, the majority of slags are processed by physical means, namely water granulation, pelletizing, air cooling, or dry granulation. These methods are discussed here.

Air Cooling

Traditionally, metallurgical slags have been air cooled in slag pots or large yards. Slag pot cooling is a slow process thus allowing crystallisation of various mineral phases as well as separation of metallic and matte phases into droplets. The slag that is poured into pits is cooled by air and sometimes by sprayed water. Partial recovery of valuable metals from slag is occasionally carried out by crushing, grinding, and metal separation through floatation, magnetic separation or leaching. The majority of slag cooled this way is, however, is only excavated and used as low-cost construction materials, or is landfilled. The major drawbacks with this method of slag handling are low value of the product, significant energy demands for subsequent crushing, and slow cooling. Further, investment in equipment and heavy machinery is required.

The slow cooling associated with this method demands a large slag-cooling area. To address this issue, several unsophisticated methods have been adopted by some steel producers. For example, at ArcelorMittal Americas, slag is sprinkled with water while stirred with front-end loaders for accelerated cooling [13]. Nippon Steel introduced instantaneous slag chill (ISC) process [14, 15] in which slag is poured into steel boxes and cooled in a sequence of steps by sprinkling water, immersion in water, and further water spraying. This method and its variants have been adopted by several steelmakers around the world. For example, in the box-tumbling method (referred to as BSS), in addition to water spraying, steel balls are mixed with slag in a tumbling box [15]. In addition to improved cooling, size reduction of slag is also achieved due to the mechanical impact.
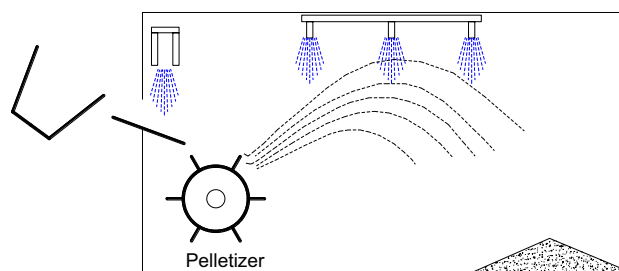

Fig. 2 Schematic of slag pelletizing process (color figure online)

Pelletizing

A small portion of blast furnace slags is converted into lightweight aggregates for use in concentre in a process known as expansion or foaming. The slag is expanded using water sprays just before it is poured onto a rotating drum, and broken up to particles typically in the range of 1–10 mm [16], Fig. 2. The break up is due to both the centrifugal force of the drum and the specifically positioned throwing vanes. Particles are cooled with the aid of sprayed water. Although the product is aimed for use as concrete aggregate, increasing the rotation speed of the drum (to make the particles smaller) and more intense cooling can produce vitrified BF slag which is ground and used in cement making.

Granulation

Granulation is the most widespread method of slag handling, employed to a number of metals as well as practically all metallurgical slags such as copper [17], ferroalloy [14, 18], and steel [19, 20], and most widely for the BF slags [1]. The principal reason for granulation is to achieve high cooling rates despite the low thermal conductivity of slag by decreasing the heat transfer length (size of particles), and increasing the surface area to volume ratio. The other advantages associated with granulation include improved easier handling of the product, reducing subsequent grinding needs, and the ability to vitrify the slag on cooling. Formation of the glassy phase is advantageous when the slag will be used as a substitute for clinker in the Portland cement or when high resistance to leaching of metal oxides in the slag is required. When molten iron blast furnace slag is rapidly quenched, it forms a solid product which is > 95% amorphous in structure. This material has high cementitious property and can replace up to 70% of clinker in Ordinary Portland Cement (OPC). Given the huge market (over 2 billion tonnes per year) for OPC, demand for the fast-cooled or ground-granulated BF slag has been high and growing rapidly in developing countries.

The fayalite-type slags produced by the copper/nickel smelting and converting processes are not strongly

cementitious without addition of CaO, and their uses include abrasive material for sandblasting and ball milling. To use such slags for construction of roads or similar applications, their resistance to leaching must be increased considerably. It is known that oxides of heavy metals such as arsenic can be locked in the silicate structure of rapidly cooled fayalite slags. In contrast, the slow-cooled slags can have considerably lower resistance to leaching of such metals [21] when mild acetic acid is used as in the TCLP (Toxicity Characteristic Leaching Procedure). In contrast when hydrochloric acid (1 mol/L) was used for leaching tests, the slower cooled and more crystallised slags showed stronger resistance to leaching of heavy metals such as As and Pb [22].

The granulation processes employ mechanical impact or high-pressure fluids (e.g. air or water) to break up the slag into small granules of typically 1–5 mm. There are several different methods to granulate or atomise the slag, which can be categorized broadly into the *wet* and *dry* granulation methods. In the following section, an outline of the various granulation processes is provided.

Wet Granulation

The most commonly used process for melt granulation uses water jets. In water granulation, the liquid slag is quenched as quickly as possible with a large quantity of water. This fast quenching ensures the highest glass content in the solidified product. For fast heat transfer and quenching, it is important to disperse the molten slag into small droplets very quickly. This break-up of slag into fine droplets is achieved by allowing the molten slag to fall through a stream of high flow rate, and in some cases high-pressure water jets, in the granulating/quenching tank at the end of the slag runner. These slag droplets need to be immersed in the high turbulence flowing water for 10 s before they have cooled down sufficiently. The thermal stress caused by rapid quenching and solidification results in the further break-up of the solidified granules into finer fragments, which could be porous in structure. The porous structure in iron blast furnace slags is at least partly caused by the reactions between the water vapour and dissolved sulphur in the slag. These reactions also cause formation of H_2S and SO_2 at the slag-steam interface and hence emission of H_2S and SO_2 with steam.

As a market leader, Paul Wurth offers two types of water granulation techniques, which are illustrated in Fig. 3. Both techniques work well, and they produce different size distributions of solid slag particles [23]. The granulated slag and water are then transferred to dewatering units. There are several different types of dewatering systems. The INBA by Paul Wurth uses a rotating drum, where the outer circumference of the drum is equipped with a screen for dewatering. During the dewatering process, the screens are cleaned with air and water. Some typical figures for the size and flow rates
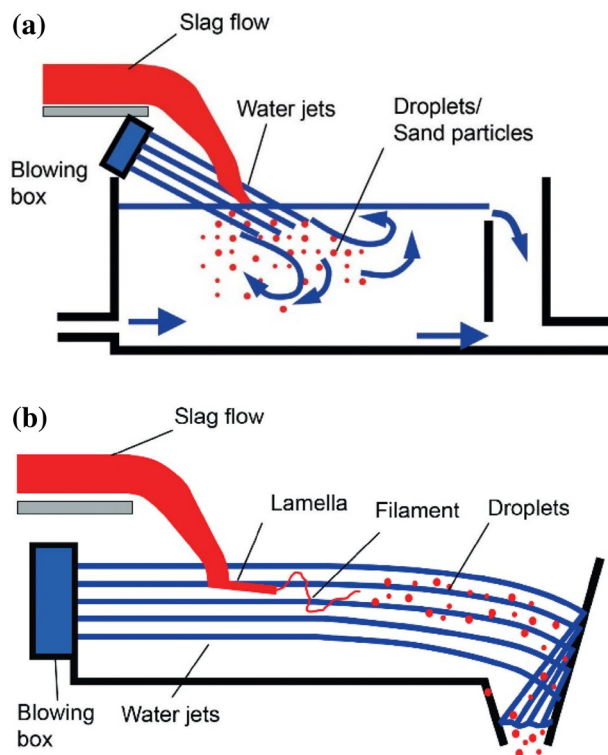

Fig. 3 Schematic of water granulation process in **a** granulation basin and **b** cold runner tank [23] (color figure online)

are reported in the papers by Paul Wurth [23]. Other dewatering systems are reported by Primetals [24] and Danieli Corus [25, 26].

Broadly, the fundamental difference between all wet slag-granulation processes revolves around the mechanical means used in the separation processes. When comparing Primetals' RASA and Paul Wurth's INBA the comparison is between the combination of screw and small drum filter vs large drum filter.[1] This difference in size of the drum is considered to be a major advantage regarding maintenance needs around the plant when in operation.

The RASA screw is very simple, and as a result, it is claimed to be an almost maintenance-free piece of equipment. Over time, screw helix plates wear down and need replacement, but this is a longer-term maintenance action. Both of the systems' drum filters require active maintenance. Relatively speaking, the maintenance needs of the INBA drum is greater because the drum is larger.

Danieli Corus tends to use a simpler filter-bed system for dewatering the granulated slag, Fig. 4. This seems to perform well with high reliability and low maintenance. This

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[1] Although the RASA flowsheet may have one extra stage, this extra stage ensures superior water quality in circulation when all other factors are considered.
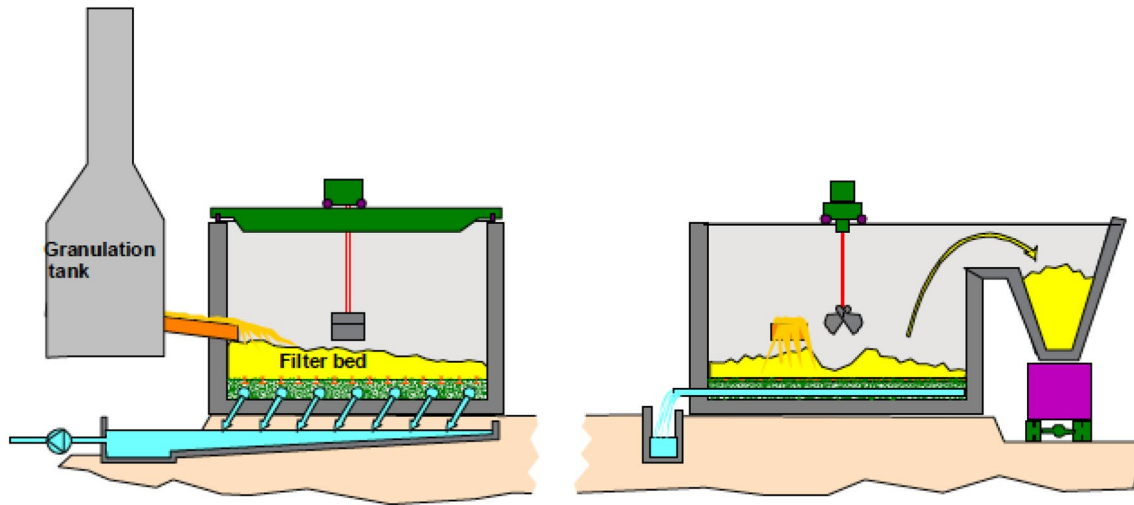
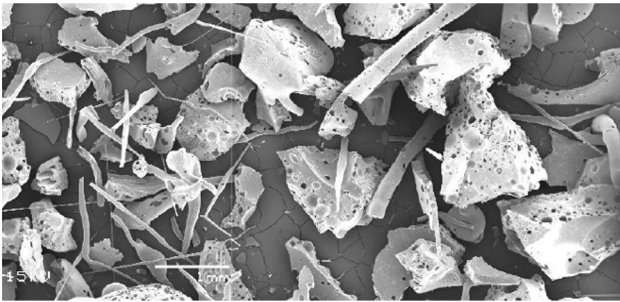**Fig. 4** The OCP filter bed dewatering system used by Danieli Corus [25] (color figure online)

Fig. 5 Micrograph of water-granulated BF slag, showing the granules structure and fine pores [25]

Fig. 6 Effects of water/slag ratio, water temperature and pressure on the residual moisture level in water-granulated BF slag [24]

system would comprise large rectangular concrete tanks (30 m × 15 m) with coarse gravel in the bottom and a network of draining pipes that collects the water underneath. The dewatered slag is removed by grab crane. In some recent installations, Danieli Corus have used dewatering wheels, which are 4–5 m in diameter and lined with steel mesh. These units are more compact than the concrete tanks.

In most water granulation systems, a large volume of water used is recovered, treated and recycled to the granulation unit. The post-treatment process includes removing dissolved sulphurous species by neutralisation, filtering and cooling. The cooling of water from 95 to 30 °C has some marked effects on reducing the amount of water that evaporates during the slag granulation as well as the emission of H_2S and SO_2. Without water cooling, evaporation loss is about 1 m^3 of water per t slag whereas with water cooling, this drops to about 0.7 m^3/t slag. Water cooling also significantly reduces the corrosion rate of the equipment. Additional information on the water requirement and recycling rates are reported by Paul Wurth [23] and Daniel Corus
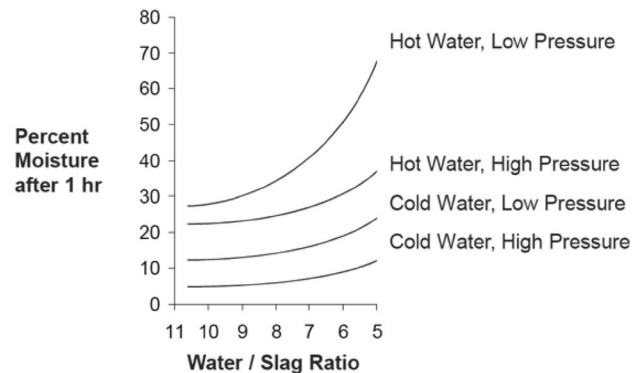
[25, 26]. Similarly, further descriptions of the dewatering systems used in INBA, RASA and Daniel Corus are reported in the literature [23–26].

The moisture level of the dewatered granulated slag is generally between 10 and 15 wt%. This represents another significant source of water loss as most of this water is locked in the fine pores and cannot be easily removed (Fig. 5). Typically, a combination of grinding and thermal treatment is used to remove the remaining moisture and obtain a fully dried product. It is worth pointing out that as the ratio of water to slag in the granulation process decreases, the moisture content of the dewater slag granules increases. As shown in Fig. 6, a similar observation has been made with respect to the water temperature and pressure [24].

The primary energy-consuming components of the water granulation processes comprise the pumps, filters and conveyers. Overall power consumption ranges between
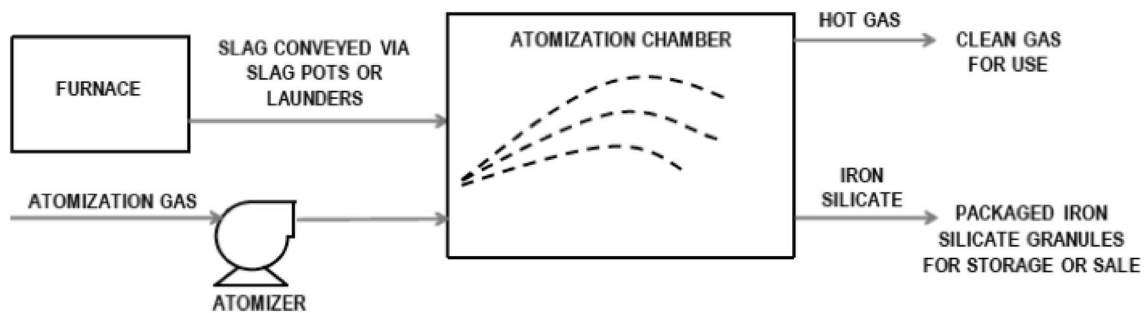
Fig. 7 Schematic process flow diagram of the air blast dry slag atomization technology [32]

5 and 10 kWh per tonne of slag processed. The economics of alternative water granulation processes have not been reported in the literature. The limited information gathered suggests considerable differences in operating and maintenance costs of wet granulation processes supplied by different suppliers.

Conventional water granulation of slag has some shortcomings when measured against increasingly stringent requirements for sustainable operations. As a "wet" process, water granulation cannot recover high-grade waste heat from molten slags. Further, the process consumes a large amount of water and may emit acid mist, H_2S and SO_2, causing serious air pollution. The wet granulated slag also has to be dewatered at a significant cost then dried. As such, alternative slag granulation methods are highly sought after to meet the current and future needs of the metals industry.

Dry Granulation

The concept of dry granulation was proposed in 1970s, a number of methods have been put forward, and some tested and trialed at pilot, demonstration, and industrial scales. These include (1) air blasting, (2) rotating drums and (3) spinning disc/cup. A fourth approach has been developed recently, which comprises injection of small steel spheres to absorb heat from the molten slag.

Air Blasting Mitsubishi Heavy Industries developed this method in collaboration with JFE (formerly Nippon Kokan KK) in 1970–1980s [27–29]. Air blast granulation involves pouring/tapping molten slag at a controlled rate to a gutter and spreading slag flow as a film. This slag is subsequently broken up and atomized by the main nozzles from underneath. The side and top nozzles control scattering, while flying slag particles (droplets) are collected in a heat exchanger chamber. In the NKK process, boiler tubes are attached to the walls or embedded in the chamber to extract heat while hot slag granules are collected and moved to discharge exit. Slag products are screened and may be used as cement feedstock, abrasive material, fine aggregate for mortar and

moulding sand. The air blasting/atomisation system requires significant amounts of compressed air and hence energy to break up molten slag into fine droplets. Such high volume of air would cause the exit temperature of the air to be lower than optimal. Thus, only a medium–low grade of heat is recovered from the molten slag.

The process was tested at industrial scale for both blast furnace and basic oxygen steelmaking slags with some success. However, the process was not successfully commercialized until recently. In recent years, Ecomaister and Hatch [30–32] have been successful in further development and commercialisation of this technology, schematically shown in Fig. 7. In their process, molten slag is atomized into a chamber using high-pressure air jet. Depending on chamber design, the hot gas from the atomizer could be recovered and used. It is claimed that 50–70% of the heat could be recovered and could be used for drying and preheating materials. However, the hot air may be at temperatures below 600 °C, hence it will be a medium–low-quality heat. It is also claimed that the process has been used to atomize mattes and alloys. Currently about 20 commercial scale dry granulation plants have been installed with two of them having waste heat recovery, which recover 30–40% of the latent heat of the slag. This technology is gaining good acceptance by the non-ferrous industry with technology maturity of TRL9.

Rotating Drums In the 1970s, researchers from Japan proposed rotary drum dry granulation. This system comprises either a single drum or twin drums. IHI and Sumitomo Metal Industries in Japan worked on a single-drum dry granulation process from 1974 to the 1980s [33–36]. This process involved pouring molten blast furnace slag onto a rotary drum which caused the slag to be broken into droplets. These droplets were collected and mixed with sand and cooled to solidification by air in a fluidized bed. The granules were then transferred to a second cooler to recover the remaining heat before discharge. Hot air produced was delivered to a boiler to produce steam. This process recovered 60% of the waste heat in form of heated air at 500 °C. The granulated slag were less than 10 mm in diameter and
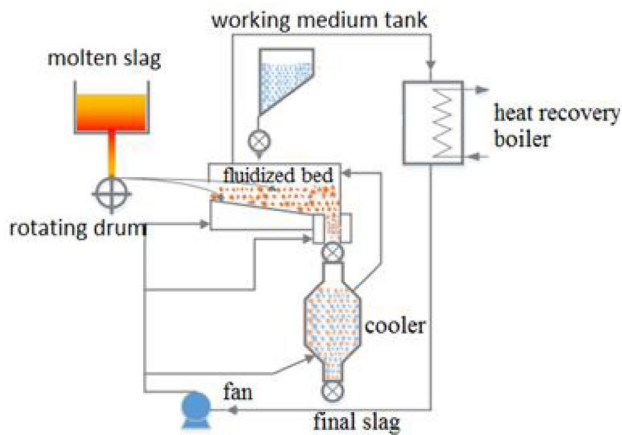
Fig. 8 Schematic flow diagram of rotating single-drum-granulation process developed by IHI and Sumitomo [36] (color figure online)
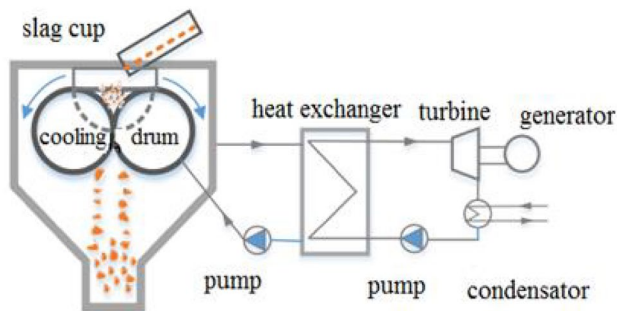

Fig. 9 Schematic of NKK Twin drums dry slag-granulation and heat recovery process [28] (color figure online)

Fig. 10 Schematic of molten slag granulation (by spinning cup) and heat recovery process by fluidized bed after Pickering et al. [7]

their glass content were lower than that required for cement production, thus were suitable for lower value application e.g. concrete aggregate. Due to this limitation, it was not commercialised.

The twin drum process was proposed by NKK in the 1980s [28]. This process was originally proposed to treat blast furnace slags to recover heat and produce glassy slags. Molten slag was poured into the space between the two drums, which rotated outwards to freeze a layer of slag on the drum surface. Slag heat was recovered through a coolant circulating through the drums. The recovered heat was then delivered to a boiler to generate steam. A plant trial was carried out at NKK Fukuyama Works. The process recovered only 40% of the waste heat from slag, while the glassy content in the slag products varied widely depending on operating condition and did not reach 80%. Schematics of drum-granulation processes are presented in Figs. 8 and 9.

Spinning Disc/Cup Compared to other dry granulation approaches, spinning disc granulation is perhaps the most-developed process. Research on spinning disc granulation
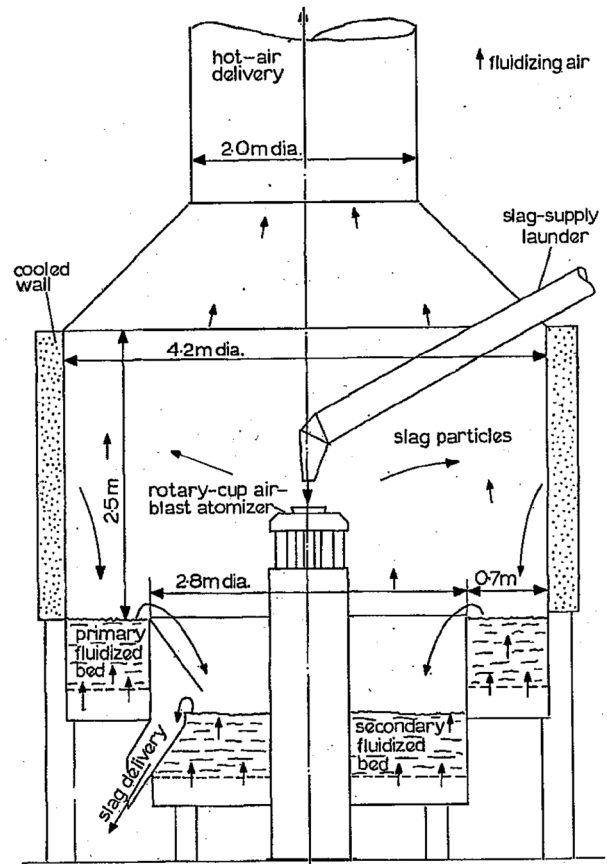
has been ongoing since the 1980s by multiple research groups in several countries. Yoshinaga and colleagues from Sumitomo Metal Industries and IHI first reported their spinning disc granulation method [29] in 1982. In 1985, Pickering and colleagues reported a spinning cup method from British Steel and University of Nottingham [7]. Driven by the energy crisis in the late 1970s, both studies were primarily aimed at maximizing heat recovery from slag. Whereas the Japanese studies provided some preliminary results on disc dry granulation, the British studies provided a plant design for both dry granulation and heat recovery (Fig. 10). In this design, molten slag enters the vessel through a launder and is delivered to the spinning cup and atomized. Flying slag droplets are rapidly cooled and substantially solidified before hitting the water-cooled wall. Hot granules are collected and further cooled through two cascading fluidized beds. Heat is recovered from the slag in the form of hot air or steam generated by boiler tubes embedded in the fluidized beds.

Although Pickering's plant design for combined dry granulation and heat recovery was only a proposal, Davy McKee, and then VAI-UK [37–39], continued development
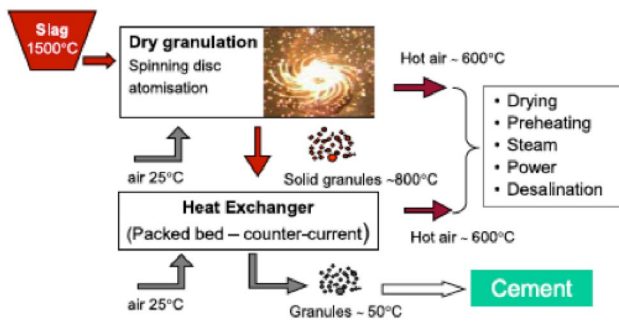
Fig. 11 Conceptual process flow diagram for CSIRO's integrated dry slag granulation with heat recovery [39] (color figure online)

Fig. 12 The semi-industrial scale (3 m in diameter) integrated heat recovery and dry granulation pilot plant at CSIRO [40] (color figure online)

of spinning cup dry granulation but without heat recovery. Their dry granulation process was scaled up to plant trials in UK and several other countries. However, the process was not commercialised for three primary reasons:

- Durability of spinning cup,
- Production of slag wool, and
- Handling of hot granules collected.

More recently, two independent groups have further developed the spinning disc/cup technique: CSIRO [39–41] and Siemens VAI technology (now PrimMetals Technologies) [42, 43]. CSIRO's focus was on addressing the technical issues that prevented the commercialisation of this technique which included improving the durability of the disc, reducing slag wool formation and reducing the size of the unit to produce high-grade heated air for various applications. CSIRO used computational fluid dynamics to optimise disc design, granulation of slag, heat transfer etc. As shown in Fig. 11, the CSIRO Dry Slag Granulation (DSG) process

involves two steps: (1) generation of solidified granules, and (2) recovery of residual heat from the granules using a moving packed bed heat exchanger (Fig. 12).

CSIRO's development of the DSG process has been piloted and scaled up to a semi-commercial scale of 3 m in diameter processing 0.1 t/min of slag. The designed disc performs well, producing granules less than 3 mm and almost no slag wool. The granulated blast furnace slag produced by the pilot plants at CSIRO was over 98% glassy and denser than the water-granulated slag. Sulphur losses from the slag were negligible.

CSIRO has partnered with Beijing MCC Equipment Research & Design Corporation (MCCE) to scale-up and commercialize the DSG process. A larger scale pilot plant has been constructed in China, which comprises a 5 m diameter granulator capable of processing 300–500 kg/min of slag. Promising early results have been obtained from this pilot plant.

In 2015, Siemens VAI Technologies (now trading as Primetals Technologies) restarted development of their dry granulation process with heat recovery through a large-scale pilot/demonstration plant at Voest Alpine Stahl (Fig. 13). In these trials, blast furnace slag is delivered onto the spinning cup, which atomises the slag to form a glassy product with over 95% glass content which is suitable as a substitute for clinker in Portland cement. The hot slag granules then fall into a modified fluidised bed where waste heat is recovered at 400 °C. Waste heat recovery at higher temperatures is possible, but requires additional optimisation. Pilot trials at 30–40 t/h of slag have shown the energy recovery to the hot air of 70% [44].

The Primetals DSG plant at voestalpine has been out of operation from April till mid-December 2018. This was wholly related to the relining of BF#A at voestalpine. Primetals had to partly dismantle the DSG plant to allow the rebuild to take place. However, they used the time efficiently to allow for some plant modifications based on the lessons learned during the first phase of operation. The plant was then hot commissioned in mid-December 2018. The first campaign was a success. They intend to continue to run campaigns with the agreement of voestalpine [24]. The key fact to note is that the product quality of the dry granulated slag is excellent compared to the wet product previously obtained at voestalpine. They have been achieving the same cementitious properties as seen in the laboratory, but now as tested in a large scale which is a major advance compared to others [44–46] The main focus of the upcoming campaigns is the reliability of operation and process control.

The denser granules produced by dry granulation appear much darker in colour with little or no pores. Interestingly, grinding these granules causes a change in their colour as shown in Fig. 14 below. The shape and density of dry
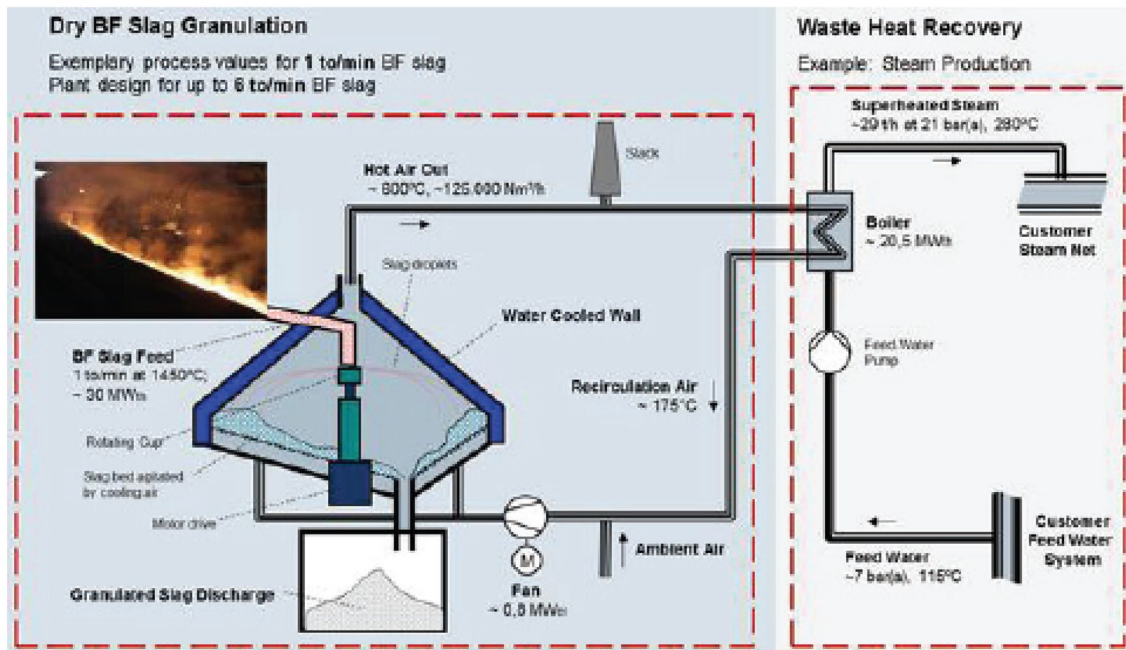
Fig. 13 Process flow diagram for SVAI/Primetals Technologies' dry slag granulation system with heat recovery and steam generation [42, 43] (color figure online)

Fig. 14 Samples of wet and dry granulated iron blast furnace slag [39] (color figure online)

granulated slags suggests superior performance in applications such as sandblasting and supplementary grinding media.

Steel Sphere Injection Paul Wurth has approached the dry granulation with a fairly simple and effective mixing method. The basic principle of their mixing method is to pour the liquid slag into a mould of slag caster. Steel spheres are added evenly over the surface of the liquid slag (Fig. 15) in the mould, which, due to their higher density, penetrate the slag surface. These steel spheres act as cooling media

Fig. 15 Paul Wurth's dry granulation pilot plant—cooling of slag with steel spheres in the mould [48] (color figure online)

and absorb the latent heat of the slag. Due to the high contact area between the steel spheres and slag, the slag is cooled fairly quickly to temperatures around 650 °C, which is well below solidification and glass transition temperature of the slag [47, 48]. In the subsequent step, the ingot (which comprises the steel spheres and solidified slag) drops onto an
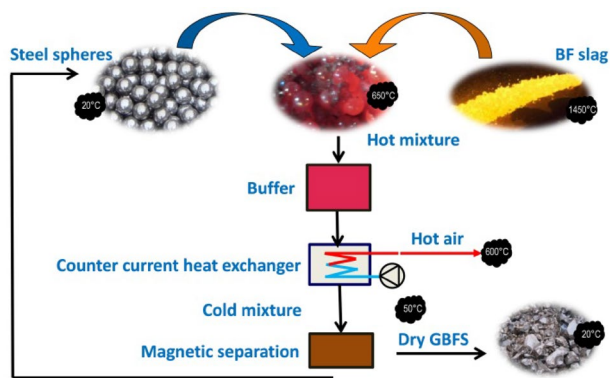
Fig. 16 Paul Wurth's concept of dry granulation of slag using steel spheres [47] (color figure online)

impact plate. The ingot disintegrates into slag particles and steel spheres with large surface area for heat extraction and recovery. The steel spheres are then separated from the slag particles through a magnetic separation step before being reused, Fig. 16.

Paul Wurth piloted this process at a full scale at the Dillinger Hutte steelworks in Germany. In November 2013, this pilot/demonstration plant was successfully commissioned with a slag-casting rate of 2.5 t/min reported. The granulated slag had high glass content but lower than the levels obtained from small-scale tests [48]. Heat recovery was planned for the second phase of the development. Due to inadequate glass formation in the slag by this process, it may be abandoned at least for slags destined for cement production. However, there is interest in the application of this technology for non-ferrous slags, where the market for the product does not require very high glassy content [45].

Heat Recovery from Metallurgical Slags

Recovery of waste heats has been of significant interest in the metals industry due to the large amount and/or high quality of the waste heats present in off-gas, dust, slag, and process cooling water. However, the recovery of energy from slag has been developed the least due to several barriers:

1. Low thermal conductivity of slag, hindering heat extraction rate at sufficient rates.
2. Corrosive nature of slags.
3. Intermittent supply.
4. Low value of energy against the substantial capital requirements.

5. Conflicting requirement for amorphous slag (vitrification vs heat recovery).

The energy recovery methods from slag may be categorized in a variety of ways; Barati et al. [1] have divided these methods broadly into the broad *Thermal*, *Chemical*, and *Thermoelectric*, as will be discussed below.

Thermal Methods

The thermal energy recovery methods are those in which the heat of slag is transferred to another medium such as air, steam, or solids added to the slag. The transfer of heat to a fluid such as steam or air allows subsequent use of the heat where thermal energy is required (e.g. space heating, materials preheating/drying, etc.) or electricity generation. The thermal methods are the most widely researched approaches amongst all the proposed routes, and are on the verge of commercial adaptation. While principally the purpose of all of these methods is rapid and efficient heat transfer from slag to the fluid, there is an array of different technologies in various stages of development. The differences are in the mode of heat transfer (i.e. direct heat transfer between slag-fluid or indirect heat exchange), the method of slag atomization (i.e. mechanical or air blast granulation), or the fluid type (air/steam/salt, etc.). In "Dry Granulation" section of this paper, the heat recovery methods that are tied to granulation were discussed. In summary, spinning disk/cup and air blast atomization are the most-developed methods and are being or just about to be tested at a commercial scale.

A study to evaluate the methods in terms of specific energy required for granulation, heat recovery efficiencies, and capital/operating costs is site-specific, also there is little practical data to allow a solid comparison. One of the few assessments on the economics of energy recovery using CSIRO's spinning disk method and using a 300,000 t/year slag-processing plant as the basis presents the following attractive figures [41].

- Operating cost 4.80 A$/t slag
- Capital cost 9.1 million A$
- Process credits compared to wet granulation: 15.72 A$/t slag
- Process credits compared to air-cooled slag: 59.79 A$/t slag

Scattered data show HREs in the range of 40–70%, with most data hovering around 50%. A challenge in this regard is the fundamental trade-off between the heat quality and the degree of slag vitrification, which is critical for BF slags. Figure 17 shows the expected variations of these parameters with air-to-slag ratio in a process involving air cooling of slag granules. While a large amount of air is required to
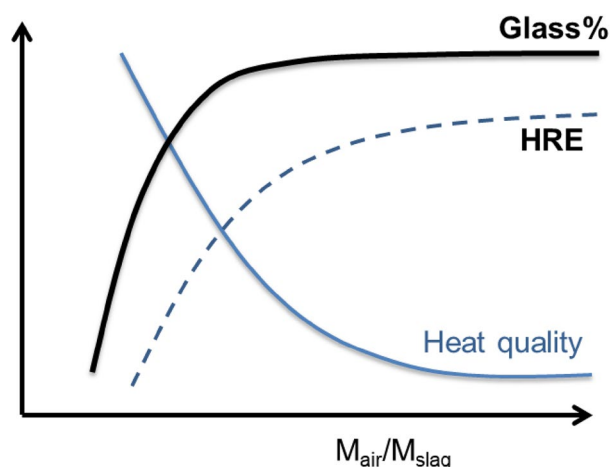
Fig. 17 Effect of air:slag on heat quality, HRE, and amorphous phase content in slag cooled in a stream of air (color figure online)

produce an amorphous slag, this would result in lower air temperature (i.e. heat grade). Fundamental studies have been carried out to determine the critical cooling rates (CCR) of slag so that the minimum amount of air is used [49].

Among the thermal methods, a simple approach not involving granulation includes the use of slag heat to melt/heat other materials injected into the slag, so that its composition is adjusted for subsequent use in specific products such as slag wool or glass ceramics [50–52]. In this approach, the heat is not recovered into another media, but is realized as energy saved elsewhere. Yang [53] reports energy recovery efficiency of 80% by mixing fly ash and BF slags to produce slag wool. The high efficiency is expected noting the direct heat transfer between the phases. This appears as a promising method but has only been applied to BF slags which already have a high-value application in cement. Further, the market for such products is not large enough for consuming a sizable amount of slag.

A detailed evaluation of the cost and benefits of any heat recovery method is necessary based on the slag type and rate, target by-products, energy value to the plant and consumers, and processing costs. For example, the limitations

of dry granulation could be the inability to recover iron from steel slags, post granulation. On the other hand, controlling the granulation atmosphere to promote the formation of desired minerals such as spinels of iron, magnesium, and chromium is an unexplored opportunity. Slag processing (e.g. granulation) coupled with heat recovery should be viewed as a new paradigm with new challenges and opportunities; an area that the metals industry would require a significant investment in.

Chemical Methods

The past two decades have seen a stream of research in converting the thermal energy of slag into chemical energy through endothermic chemical reactions. The concept of all these methods is to utilize the sensible and/or latent heat of slag for an endothermic reaction such as calcination of limestone or dolomite, reforming of methane with steam or CO_2 [54–58], gasification of coal with steam/CO_2 [59–68], pyrolysis of coal, waste plastic or biomass [69–73], or reduction of CO_2/H_2O [74–77], as outlined in Table 3. As a result, the energy may be later recovered by combusting the obtained fuel, or is saved in the first place by eliminating the need to use an external source of energy in processes such as lime calcination. A thermodynamic evaluation of various reactions by Akiyama et al. [56] has rated decomposition of limestone, reforming of methane, and gasification of carbon as the reactions with the least exergy loss, hence most energetically efficient. Generation of fuel from reforming of hydrocarbons or reduction of CO_2/steam with slag constituents has been of greater interest. This is due to the versatility of potential uses for the product as fuel or chemical, and ability to transport the energy (e.g. fuel). It is worth noting that slag in such processes may play a role greater than the heat source only, by facilitating the reactions as a catalyst, or being involved in the reactions as a reductant (e.g. reducing steam to H_2).

Practically, all the above studies have been carried out on blast furnace slags, with a few on steel slags. Further, there is very limited information on the energy conversion efficiency of such reactions as some works are only conceptual

Table 3 The proposed methods for converting slag heat into chemical energy

Purpose	Primary reaction
Methane reforming [54–58]	$CH_4 + H_2O \rightarrow CO + 3H_2$ $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
Pyrolysis (Coal, Biomass, Waste Plastic) [69–73]	Solid $\rightarrow C +$ Gases (CO, H_2, C_xH_y, etc.)
Gasification of Coal/Biomass/Municipal Waste [59–68]	$C + H_2O \rightarrow CO + H_2$ $C + CO_2 \rightarrow 2CO$
Reduction of H_2O/CO_2 [74–77]	$FeO + H_2O \rightarrow Fe_2O_3$ (or Fe_3O_4) $+ H_2$ $CaO + V_2O_3 + 2\ CO_2/$ $\quad H_2O \rightarrow (CaO)_3(V_2O_5) + 2CO/H_2$

Any imbalance is due to use of slag from storage or imports

with thermodynamic calculations and the others have been performed in a laboratory scale and under isothermal conditions. In addition to the state of development, the chemical energy recovery methods are associated with major shortcomings as described below.

The energy efficiency in chemical methods cannot certainly exceed those of commercial methane reforming (using fuel heating) at 70–85% [78], or 40–60% for biomass gasification [79]. This is because such reactions are favoured at temperatures typically above 500 °C for gasification and above 800 °C for methane reforming, thus only a small portion of the slag enthalpy over its cooling temperature range may be effectively utilized. As a result, the overall energy efficiency of such processes is estimated at 25–50%. Noting if the end use of the produced fuel is a thermal application, other losses would occur at that stage, rendering the efficiency even lower.

For BF slags with the end use as cement clinker, the cooling rate of slag should be fast enough to prevent crystallization, as soon as the temperature approaches the slag melting point. This has been estimated to be tens of degrees per second, as shown in Fig. 17. On the other hand, the rate of heat extraction in chemical methods could be limited by the rate of reaction on slag, and as a result insufficient to achieve these rates. Further, the amount of reactants compared to slag mass is small (for example, 1 tonne of methane and steam for every 10 tonnes of slag [1]), which cannot extract the slag heat fast enough. The heat recovery from slag may then be divided into three regions according to the TTT diagram. Above the melting temperature (Zone 1 of Fig. 18a), the cooling may take place at any rate and the reaction rates are high, thus a suitable range for an endothermic reaction. However, this is a relatively narrow temperature range, hence recovery of a small fraction of the slag heat. Between the melting point and TTT nose temperature (Zone 2), rapid cooling is required, which may not be realized through a chemical reaction only and other "thermal" methods should supplement or solely carry out the heat extraction. Finally, below the TTT nose (Zone 3), cooling can take place at any rate, making the chemical methods suitable again. However, the use of slag heat below the TTT nose temperature is not effective as the temperatures are low for some reactions (e.g. reforming), also the catalytic effect of amorphous slag at these temperatures is weak [80, 81]. In essence, this leaves only a small temperature window where the slag heat can be effectively utilized to carry out endothermic reactions. It is possible to use the heat of slag in a larger range to only heat up the reactants, but that would be considered amongst "thermal" methods, and would require a complicated technology with a combination of heat exchangers, chemical reactors, etc.
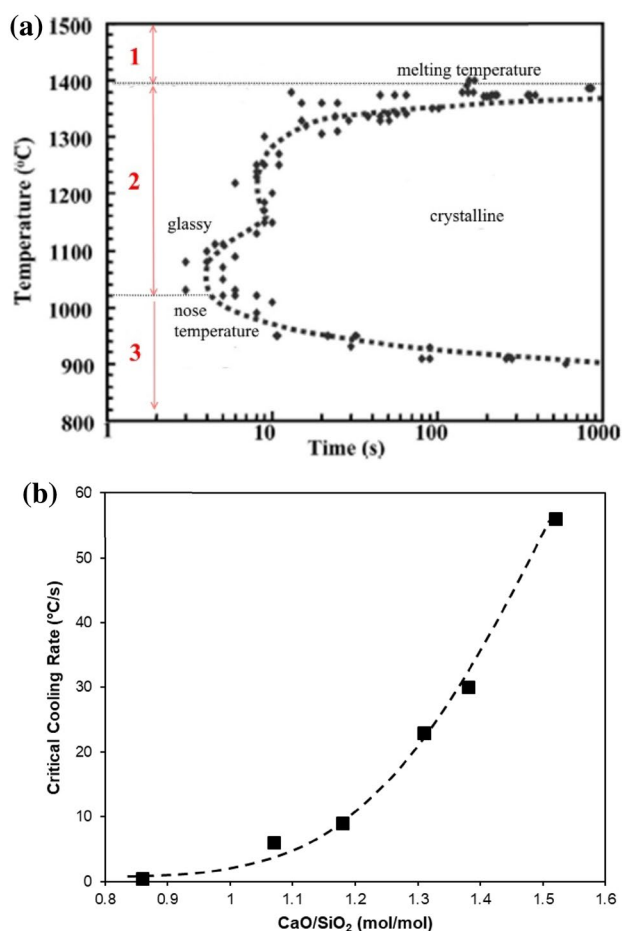
Fig. 18 **a** TTT diagram of BF slags, modified from Ref. [82], and **b** critical cooling rates of CaO–SiO$_2$–Al$_2$O$_3$–MgO slags [83] (color figure online)

For slags containing transition or base metals (e.g. steelmaking slags), rapid cooling is often not a requirement, and therefore, the heat may be recovered over the entire cooling range. However, direct contact of reactants (e.g. methane or coal) with slag would result in the reduction of some metal oxides such as FeOx, consuming the reactants for purposes not intended for, and producing a partially reduced low-grade material which has no uses in the industry unless ground and separated. Again, this would create a complex flowsheet with many steps which would be difficult to justify economically. Indirection heating of reactants is an option here, by exchanging the slag heat to the chemicals through a heat exchanger or another inert media. This would make such methods comparable to the thermal methods with additional steps for handling the produced fuels.

In summary, it appears that recovery of slag energy by chemical methods could be complicated for BF and steelmaking slags and necessitates several cooling regimes with different rates or indirect heating of reactants, additional slag separation and chemical handling steps. The investment in

such technologies would be greater than the thermal methods due to the multi-step process, as well as the need for safe handling of explosive and/or toxic gases. Finally, the ultimate energy recovery efficiency after all conversions will be lower than the thermal methods. Consequently, it is not expected that such methods will play a significant role in the future of slag energy recovery.

Thermoelectric Conversion

A fundamentally different approach for recovery of waste heat involves the use of thermoelectric materials for direct conversion of heat to electricity, referred to as Thermoelectric Generation, TEG [84]. The TE devices rely on semiconductor materials that produce a voltage when exposed to a temperature gradient through the Seebeck effect. They have found a range of applications from automotive to domestic for improved energy efficiency or power generation from different heat sources such as geothermal and solar [85]. From a practical perspective, the most important performance indicator of TE devices is the conversion efficiency, which can be calculated from the figure of merit (ZT). Despite numerous advancements in the field, the highest efficiencies reported to date are in the order of 10–20% [86]. Further, the high temperature application of TE is limited to ~ 1000 °C. The thermoelectric efficiency increases with temperature for a given material but the high-temperature TE materials possess lower efficiency than those designed for lower operating temperatures [87, 88]. For example, for a SiGe-based device at 800 °C, the ZT is in the range of 0.5–0.7, giving a theoretical TE efficiency of 7–9% only.

The direct use of TE materials for heat recovery from liquid slag is practically impossible because of the above limitations, in addition to the degradation of the materials in contact with the slag. It is, however, possible to employ such devices in a lower temperature range of slag (e.g. after granulation and partial cooling). A more attractive option is to transfer the heat of slag to another fluid at a lower temperature or a phase-change material [89], matching the more practical operating range of TEG devices.

For the purpose of electric power generation, the TEG efficiencies are comparable to thermal methods. This is because of ~ 50% thermal efficiencies in such methods, 35–40% of which can be converted to electricity. Consequently, the overall conversion factor is in the range of 15–20%, which matches those of today's best performing TEG devices. The optimum technology may thus be decided by the capital and operating costs of the two technologies, on which no information is currently available.

Summary

Metallurgical slags are a major secondary resource in terms of their mineral and energy contents. The traditional ways of slag cooling are transforming into more complex approaches involving chemical modification, fragmentation, and controlled cooling for realizing the energy and materials values.

The two types of slag granulation systems (wet and dry) produce different products and require different amounts of water and energy. Their physical footprint could also vary considerably particularly when one considers the requirements for dewatering, water treatment and recycling plants for water granulation. Unlike the well-established and low-risk wet granulation technologies offered by various vendors, a number of dry granulation technologies are emerging, which offer advantages over the water granulation technologies. Dry granulation requires far less cooling water, it is more compact and allows recovery of waste heat/energy from the molten slag. Dry granulation also avoids the emission of H_2S and SO_2 with steam. The dry slag atomisation by air blasting has been commercialised in recent years and provides some attractive features.

An array of energy recovery methods have been investigated in the past five decades with a surge in research in the recent 15 years. These methods can be classified into thermal, chemical and thermoelectric generation technologies. The thermal methods are developed most and are promising decent heat recovery efficiencies in simple designs. The chemical methods offer the production of fuel from slag heat but are facing fundamental constraints, and require complex, multi-step technologies to yield meaningful energy and material recoveries. The TEG systems are suffering from low operating temperature and conversion efficiencies. For these reasons, they have not been given much attention in relation to energy recovery from slag.

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