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Innovative approaches for an optimized processing of metallurgical slags

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ABSTRACT

Metallurgical slags are produced in large quantities all around the world as a result of smelting, refining or alloying processes applied to metals, ores and recycling material. The slag phase serves different purposes in metallurgical processes. It prevents heat losses and protects the metal phases from contaminations and absorbs gangue and extracted impurities. Due to achievable metallurgical efficiencies certain amounts of valuable metal contents always remain in the residual slag. Recycling of these metallurgical slags has several positive effects, such as optimized ecological and economical compliance of the producing industry. If recycled metal contents can be reintroduced into existing processes, required inputs of raw material can be lowered. High metal prices enable the economic recovery of metal contents in metallurgical slags by applying different non-metallurgical processing methods. Conventional processing of metallurgical slags utilizes processes such as hand picking, selective comminution, screening and magnetic separation. Those state of the art processing techniques have limitations in terms of achievable metal recoveries and required energy demand. The approach for an optimized processing of metallurgical slags targets enhanced metal recoveries in combination with lower specific treatment costs. Processes such as coarse and ultrafine density separation, as well as sensor-based sorting as a pre-concentration stage are used to enable an efficient recovery of metal contents in slags. By applying these methods a completely dry working process is possible. This paper reviews the commonly used methods and describes approaches for innovative processing of metallurgical slags to enhance metal recoveries. Focus of this paper is laid on sensor-based sorting as well as on processes for dry density separation.

INTRODUCTION

In a situation of steadily increasing demand for raw materials, the issue of how to use our resources most efficiently is a contentious economic and environmental political issue today. A combination of sustainable exploitation and use of primary resources in combination with an optimized handling and processing of secondary resources, such as metallurgical slags is the key for a better handling of existing resources.

Metallurgical slags are by-products from metal extraction, refining and alloying processes and are produced in significant amounts. The slag phase is used to encapsulate impurities and additives added during casting and alloying processes for further purification of metals. Besides impurities, slags usually contain significant amounts of metal contents (Van Oss, 2002). A suitable recycling and reintroduction of such metal contents and non-metallic slag residues is highly desirable but, yet, not always applied. Besides recycling of metallurgical slags in existing processes, the recycling of old dump sites is important. If not properly recycled and reintroduced into the raw materials cycle as new products, an important resource is lost. Numerous technologies exist which differ in terms of costs and efficiency. Applied state of the art technologies for recovering metal contents from slags include, for example, selective comminution, wet and dry density separation, magnetic separation, dense media separation or combinations of the proposed techniques. However, metal recoveries, especially for fine, intergrown metal contents as well as energy and resource efficiencies are low for many applied processes. In many cases, the fine fraction is not even treated and discarded as waste material (Wotruba, Weitkaemper, 2013).

This paper reviews current application fields for metallurgical slags. Applied technologies for recycling and recovering of metal contents and non-metallic compounds, with emphasis on mechanical processing technologies are described, and new approaches for a more economical, environmentally and therefore sustainable treatment with focus on stainless steel slags on a dry basis are introduced.

RECYCLING OF METALLURGICAL BY-PRODUCTS

As metallurgical processes take place, impurities from the ores (gangue), fluxing agents, added during refining and smelting processes, as well as metal contents combine within a liquid phase above the liquid metal. Metal contents contained within the slag phase can be present as agglomerates of various alloys, oxides or as free metals (Wotruba, Weitkaemper, 2013). Besides recycling of metal contents, utilization of slags residues is an important factor which needs to be considered when treating metallurgical slags. The specific use of the various slag types thereby strongly depends on metallurgical processes, slag constituents and physical as well as chemical features and therefore defines the technical application spectrum (Reuter, Xiao & Boin, 2004; Wotruba & Weitkaemper, 2013). Recycling quotas and applications for the various slag types differ, depending on chemical compositions and physical properties of each material. Generally all slags can be subdivided into ferrous (e.g. iron making and steelmaking slags) and non-ferrous slag types (e.g. copper slags, lead- and zinc containing slags).

Compared to production rates from other slags, iron-making and steel-making slags make up for the vast majority of slags produced worldwide. Each year, more than 400 million tonnes of iron and steel slag are produced (World Steel association, 2010). Compared to the combined global iron and steel slag production, the non-ferrous slag production makes up to about 20 % of that mass (Sanchez & Sudbury, 2013).

European utilization rates for steel slag account for approximately 65 % with 35 % of the steel slag which is still being dumped (Reuter, Xiao & Boin, 2004). Steel slag can either be used as construction material or pavement material. The alternative option is to directly recycle the slag within the metallurgical process (Dippenaar, 2004). Stainless steel slag is a by-product of stainless steel making. Due to high chromium contents and poor physical properties there is almost no utilization of this slag type (Reuter, Xiao & Boin, 2004). However, different processes have been developed over recent years, which convert the stainless steel slag into usable materials by enhancing their physical and chemical properties through metallurgical modification. Larger quantities of ferroalloy slags are produced during Fe-alloying production. Products of this process include FeCr and FeMn alloys which are mostly produced in electric arc furnaces (Reuter, Xiao & Boin, 2004). Chromium content of FeCr slags usually ranges between 5 to 10 %. (Holappa & Xiao, 2004). Currently most of the ferroalloy slags produced are sent to landfill, with a small amount being used for cement production or other purposes (Reuter, Xiao & Boin, 2004). Physical properties of ferrochrome steel slags have been found suitable to be used as construction material, however, environmental impacts of the chromium bonded in the slag are not clear (Reuter, Xiao & Boin, 2004).

Another example for valuable slag types includes **lead-, zinc- or nickel- slags**. Typical Pb and Zn contents of lead- and zinc- slags vary between 1-3 % Pb and 6-17 % Zn (Reuter, Xiao & Boin, 2004). The physical treatment of such slag types however is beyond the scope of this publication.

Copper slag, as a by-product of smelting and converting processes usually contains significant amounts of valuable metals. Copper grades in slags can reach values of up to 0.8 M.-% (Zander et al., 2011). Converter copper slags are usually retreated inside the metallurgical plant, so that a maximum Cu-recovery can be achieved. Physical processing for recycling of copper slags utilizes methods such as flotation where pure Cu-metal as well as sulphide copper phases can be recovered (Wotruba & Weitkaemper, 2013). Remaining copper slag can be used for different purposes. Brindha & Nagan for example have successfully tested the applicability of copper slag for the replacement of aggregates in concrete, where copper slag could be used to replace up to 40 % of the required sand content with positive effects on the overall strength of the concrete (Brindha & Nagan, 2010). The recycling of copper slag types is however not the focus of this publication.

STATE OF THE ART IN SLAG PROCESSING

Economical reclamation of metal contents from slags is especially viable for stainless steel slags as well as for slags from steel refining (Wotruba & Weitkämper, 2013). Metal recovery from slags works particularly well, once metal contents are present as pure metals. Metals within slag particles are usually present as inhomogeneous inclusions in form of free metal components or non-liberated pure metal phases, metal oxides or metal sulphides (Wotruba & Weitkämper, 2013). Other particles contain only very low or even no metal content.

Generally, slag processing is focused on the reclamation of free metal. In the article of Jungmann and Schiffers (Jungmann and Schiffers, 2010) the main processes of steel slag recycling are described, which can be subdivided into two major approaches. First, selective crushing, handpicking in combination with sorting techniques such as magnetic sorting to reclaim coarse, liberated metal phases with low metal recovery. With this approach only coarse grain sizes are treated, with no metal recovery being conducted for fine fractions. As typically about 50 % of the metal contained in the slag is smaller than 10 mm, it becomes clear that, in some cases, significant amounts of metal are not recovered in such processes (Jungmann & Schiffers, 2010).

The second approach combines comminution and classification for metal recovery. Here, the complete material stream is ground down to liberation size and below with subsequent sieving or hydraulic classification for recovery of metal contents. Combinations of crushing, followed by several grinding stages via rod- and ball milling are used. Ductile characteristics of the metal contents are used to separate liberated metal phases from mineral slag phases. As mineral phases are ground to grain sizes of 95 % below 0.2 mm, metal contents remain unground and can be separated by classification ore screening (Jungmann & Schiffers, 2010). With this approach, metal recoveries above 95 % and metal concentrations from 90 to 92 % are practicable. However, as the entire material stream is ground to liberation size, the complete mineral phase is also comminuted and is therefore no longer applicable for construction purposes without prior treatment such as agglomeration and drying (Jungmann & Schiffers, 2010). Besides the described issues, energy and water consumption as well as machine wear are high. It should be noted that similar techniques as well as combination of both approaches are also used in steel recycling processes (Jungmann & Schiffers, 2010). Figure 1 shows a combination of both approaches by combining selective crushing and grinding, handpicking as well as sorting techniques such as magnetic sorting to regain liberated metal phases.

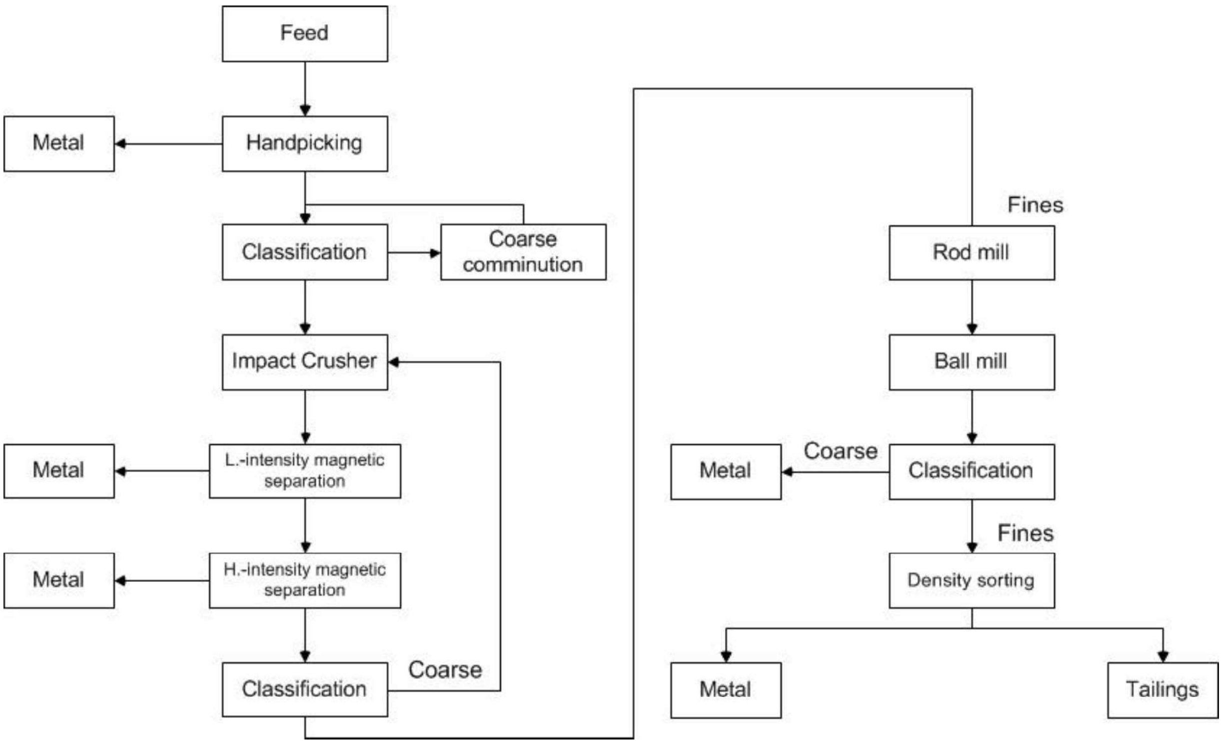

Figure 1 Wet processing route for metal recovery from slag

It becomes clear that, in this case, no pre-concentration is used for an early separation of non-metallic compounds from the slag. As a result, the entire material stream is crushed and ground down to liberation size, producing large amounts of fines which need to be treated and disposed to landfill, at high costs.

Generally, depending on the process applied, two pathways can be differentiated for recovery of metal from slags. The first way includes processes resulting in high metal recoveries, high metal grades but low recyclability of mineral slag residues from the process. The second way includes the treatment of relatively coarse grain sizes with lower metal recovery, but better recyclability of non-metallic slag residues. It shows that further work needs to be done on improving both, metal recovery and recyclability of non-metallic slag phases. In recent years, several technologies have been developed which can, if properly used, increase the efficiency of slag and recycling processes.

ALTERNATIVE APPROACH FOR PROCESSING OF METAL SLAGS ON DRY BASIS

As shown, various approaches exist which either yield high metal recoveries or good reusability of non-metallic slag residues. On a long-term view, the goal must be to keep the dumping of metallurgical slags to a minimum (Wulfert & Jungmann, 2013), for both, metal and non-metallic slag contents. In the near future, not only will the metal recovery rate be an important economic factor, but also the added value through utilization of non-metallic residues of the slag (Wulfert & Jungmann, 2013). Due to technological developments, entirely dry processing flow sheets for metallurgical slag processing are possible (Wulfert & Jungmann, 2013). The overall approach of a dry, environmental friendly and efficient reclamation of metal contents and the use of mineral slag phases for more advanced applications have been the goal of several studies conducted by the Unit of Mineral Processing AMR RWTH Aachen. The most important sub-processes for dry slag processing include the following steps: classification, pre-concentration of coarse particles, middlings and fines, further comminution and sorting of metal pre-concentrates.

Simplified it can be said that usually three products in each size fraction are produced during comminution; a metal-free product, non-liberated metal contents and free metal particles. The connection between slag comminution and products from this step is shown in Figure 2.

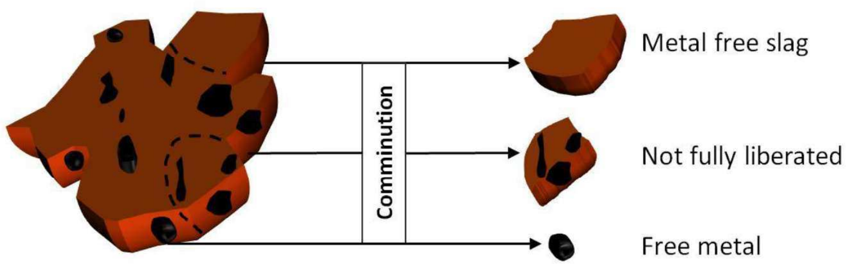

Figure 2 Schematic view of effects from slag comminution

The idea behind pre-concentration is that metal-free particles as well as pure metal should be separated as early as possible, thus reducing the mass which needs to be treated by comminution and sorting processes.

As pre-concentration stage for coarse grain sizes (approx. 30-150 mm), sensor-based sorting can be used to separate coarse metal-free slag particles at an early stage of the processing chain. This is done by utilizing electromagnetic sensors (inductive sorting). The principle of electromagnetic sensors (metal detectors) is based on the eddy-current principle. As a conductive material passes through an electromagnetic field an eddy-current is induced into the conductive material on the conveyor belt by an emitting coil. As a results of the current induced into a conductive material a magnetic field builds up, which induces a detectable current in a receiving coil (Neubert, Knapp & Wotruba, 2013). Metal recoveries at this pre-concentration stage can reach values above 90 % (Jungmann & Schiffers, 2010). In the size range of 8-50 mm, detectability of metal particles reaches values of up to 100 %, whereas detectability decreases to approx. 90 % for metal particles with grain sizes of 4-8 mm (Wotruba & Weitkämper, 2013). Metal particle sizes below 1-2 mm are, however, difficult to detect.

Not fully liberated metal contents (see Figure 2) are reintroduced into comminution circle for further liberation and fed into subsequent sorting processes. Several advantages come along with the use of a pre-concentration stage. By separating non-metal particles, less mass has to be treated in the following processes, thereby reducing machine wear and energy consumption in subsequent grinding processes. Another major advantage of pre-concentration is that less fines are produced, as only the pre-concentrates are ground for further metal recovery. Besides that, coarse separated metal-free aggregates can be used for applications in construction and do not need to be discarded.

Below grain sizes of approx. 25 mm, various technologies can be used for a pre-concentration of metal particles. Due to low susceptibility of ferrous alloys and stainless steel, dry magnetic separation can be one possible method. In addition to magnetic separation, jigging can be applied for sorting of slags, both wet and dry. With dry jigging, two products can be produced; a heavy and a light fraction (see Figure 3). The technology is applicable for grain sizes from +2 mm -50 mm. Recent investigations on stainless steel slag have shown that for dry jigging, metal recoveries of 95 % at grain sizes of 2-20 mm with metal contents of 80 % in the heavy fraction are possible.

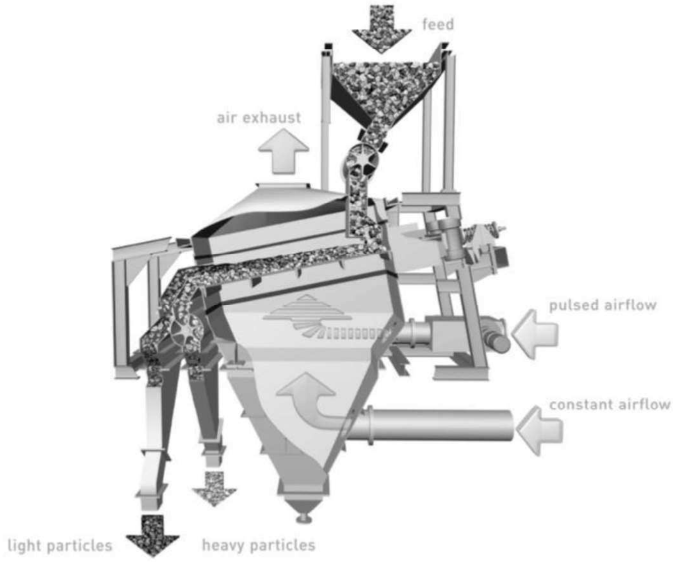

Figure 3 Schematic view working principle of air jig (Weitkaemper & Wotruba, 2010)

The result of this pre-concentration step is, again a metal-free product, metal particles and a non-liberated metal phase. If free and intergrown metal is present in the feed, cleaning the light fraction from pre-concentration stage might become necessary to increase metal recovery; this is due to the inability to produce more than two products in the air jig. Non-liberated phases are fed into subsequent comminution for further liberation, whereas metal-free particles and metal can be seen as end products.

For grain sizes below 2 mm, dry fluidized bed separation is an effective technique for pre-concentration of free metal and separation of metal-free phases from slag. Figure 4 shows the basic principle of fluidized bed density separation. Here again, metal concentrates have been produced with metal a content of 93 % at a recovery of 88 % at only 5 % mass pull to the heavy concentrate. The light fraction can be used as by-product aggregate, whereas the pre-concentrate can possibly be used as final product or ground for further liberation of metal content and is subsequently fed into another density separation for final metal recovery. Compared to wet density sorting technologies such as spiral concentrators or shaking tables, dry sorting of this fraction provides two advantages. As water consumption for sorting processes generally increases with decreasing grain sizes, large amounts of water are saved. Additionally, no water retreatment cycle is needed, thus reducing operating costs when compared to wet processing.

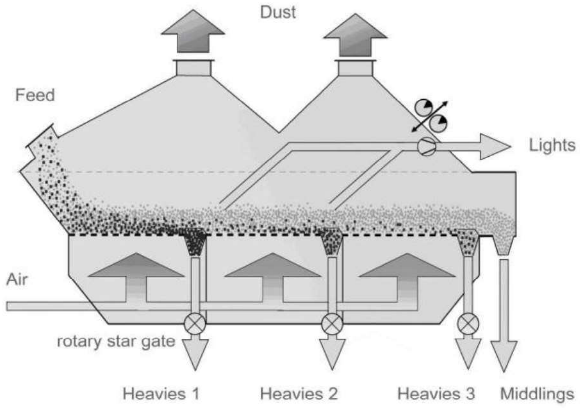

Figure 4 Schematic view working principle of fluidized bed separator (Weitkaemper & Wotruba, 2010)

RESULTS AND DISCUSSION

Results given in this paper show that, besides existing technologies, dry sorting of metallurgical slags is possible. Processes such as coarse and fine density separation, as well as sensor-based sorting as pre-concentration stages can be used to separate metal-free particles at an early stage. With this approach metal-free particles in various size ranges can be separated and utilized as valuable by-products. Simultaneously only particles with metal content are further liberated by comminution, thus resulting in a more efficient, energy and wear saving process. The presented sorting techniques can be combined to a completely dry recovery process. The combination of lower energy and water consumption, decreased wear and higher recyclability of metal phases of the slag show the large potential of dry slag processing.

Based on the results, a conceptual process flow chart, which could be used for different applications, is given (Figure 5). Main specifications include that only worthwhile material is comminuted for metal recovery, while free metal as well as metal-free particles are separated as early as possible. First, coarse metal particles (bears) are reclaimed via “handpicking”, followed by a screening of the entire material stream to provide required grain sizes for subsequent sorting equipment. Three fractions are produced, a coarse fraction (approx. + 25 mm), middlings (- 25 mm) and fines with grain sizes of approx. below 2 mm. Coarse pre-concentration is achieved by sensor-based sorting, which separates metal-free slag and free metal particles. Intergrown particles are crushed for further liberation of metal contents. Middlings from screening stage are sorted with dry jigging, which again results in a metal-free slag. Concentrates are fed into a selective crushing stage for recovery of free metals at high metal grades. The fines from screening are pre-concentrated by dry fluidized bed separation, which separates metal-free slag particles. Heavy concentrates from fluidized bed separation are combined with residues from selective crushing and fed into a selective grinding stage with subsequent metal recovery by dry density separation.

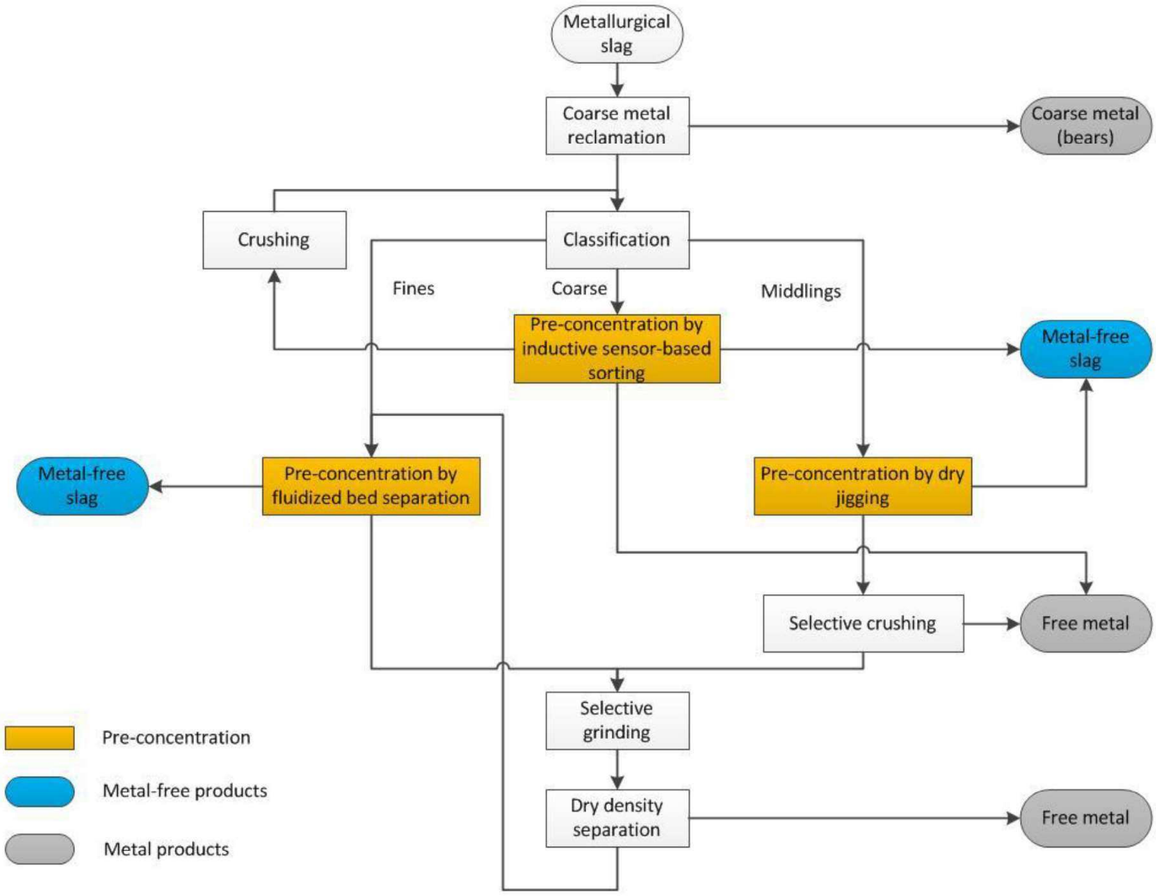

Figure 5 Simplified conceptual flowsheet for dry processing of metallurgical slags

Still, a large proportion of the slag is sent to landfill, although the metallurgical industry is directing their efforts into minimizing the production and processing of slags (Reuter, Xiao & Boin, 2004). The approach for a dry processing of metallurgical slags can be a great contribution for a more efficient, economic and environmentally friendly metal production.

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