INNOVATIVE SOLUTIONS FOR RECYCLING OF BY-PRODUCTS*

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Abstract

Government regulations around the world concerning environmental care are becoming more stringent, also including regulations and restrictions of depositing and use of dust, sludge and slag generated in the iron and steelmaking process. With this scenario, by-products such as iron containing dust, sludge, oxide fines, mill scales and slag, become a valuable resource and recycling may be a profitable activity within a plant. Up to ten percent in mass of the total steel output of dust, sludge and mill scale by-product materials and more than 40% of slag by product are generated within an integrated steel plant with an iron content ranging from 50% to 65% for fines and up to 25% for BOF-slag. Slags are being widely recycled and used in the cement industry, as is the case for BF slag, and in the construction industry in the case of BOF slags and EAF slags. However, value of BOF unmodified slag is typically low and environmental regulations limit the usage of the unmodified BOF slag. This paper describes innovative solutions for recycling of fines using cold briquetting technology and the modification and granulation of slag from steelmaking that increase the value of the by-product and yield a marketable product.
Keywords: Recycling; Briquetting; Slag valorization; Slag granulation.

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1 INTRODUCTION

Significant amounts of by-product fines are produced and collected in steel plants at all steps of iron & steelmaking. It can be assumed that per ton of steel produced around60 -150 kg of particulate by-product is generated. Considering that these by-products have an average iron content of >50%, this is 3 up to 7,5% of the total steel production.
Primetals Technologies has developed several recycling technologies for treating particulate by-products. Cold briquetting is one of the favorable solutions to transform fine material into recyclable agglomerates.

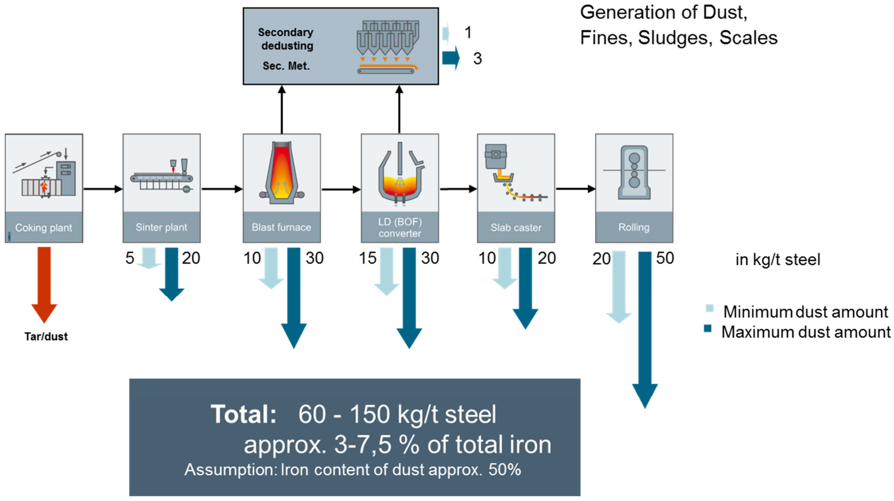

Figure 1. Typical by-product fines generation in an integrated steel mill.

The specific amount of LD slag generated is in the range of 120kg per ton of steel. Conventional uses of LD converter slag from steelmaking such as in construction or to produce fertilizer are becoming less attractive due to stricter environmental regulations, decreasing market volume and falling prices. Economically attractive methods to process and market slag, in addition to closed processes for slag modification and handling to minimize dust emissions and space requirements, are therefore gaining interest with steelmakers. A promising development underway by Loesche, Primetals Technologies and partners is the modification of LD slag so that it can be used as a cement clinker substitute.

2 RECYCLING OF FINES – COLD BRIQUETTING

Recycling of only a part of the by-product stream to the sinter plant is very common. In many cases the addition of mainly unconditioned by-products may be possible, in some cases with a negative impact on the plant operation, such as increase generation of fines and reduction of productivity, and leaving still a large amount of by-products unused.
In order to include most or all of the generated by-products, cold briquetting of various dusts and sludges allows integrated recycling within existing primary production units. After pre-treatment of the residues, including drying, screening and mixing, binders are added and following the mixture is briquetted using roller-type presses. The selection of the binder system is dependent on desired metallurgical route for the respective recycling.

In Figure 2 a block diagram of a cold briquetting process including pre-treatment of the waste material is shown.
In the first step of the cold briquetting process the wet by-products are dried. Then the dried materials as well as other dusts are mixed while adding the binders. Afterwards the material is directly fed to a briquetting press. In a final step the product briquettes are screened and then conveyed to the curing and storage yard. Approximately 10% fines are internally recycled after the screening. Final product screening is done just before loading to the trucks.

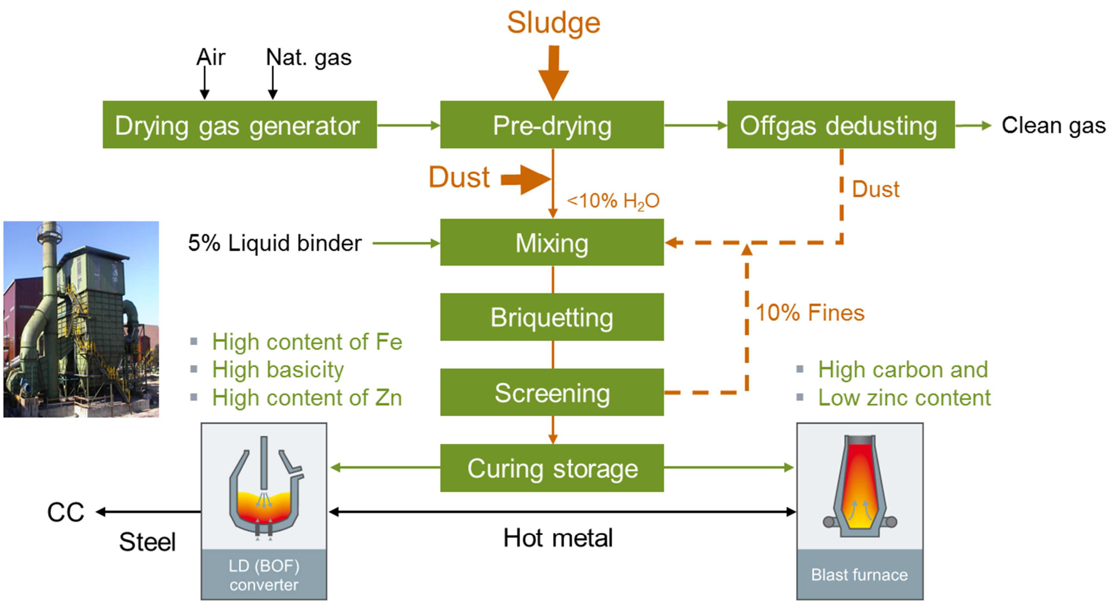

Figure 2. Cold briquetting process – Reference ILVA Taranto

The reference plant at ILVA Taranto was designed as 2-line briquetting arrangement for a yearly production of around 240,000 tons. The briquettes were foreseen to be recycled to the LD converter (BOF) and blast furnace (BF) up to certain defined amount.

LD approx. 4 t per heat (approx. 8 kg briquettes/t_{steel})
BF approx. 1% of burden

A combination of molasses and hydrated lime is used as binding agent. Following input materials are treated in this briquetting plant:

- Converter fine sludge 30%
- Converter coarse sludge 10%
- BF sludge 10%
- Mill scale sludge 25%
- Sec. LD-dust 5%
- Dust catcher dust (BF) 10%
- Separation iron fines 10%

Briquettes with a high iron content and high basicity can be charged directly into LD converter (BOF), replacing cooling scrap or ore. Briquettes rich in carbon but with limited alkali and zinc contents can be charged into the blast furnace.

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Figure 3: Product briquette

Figure 4: Briquetting plant, ILVA Taranto, Italy

The main benefits of this system are:

- Less raw materials utilization due to recycling of by-products (ore, scrap, coke) and therefore reduced operating costs
- Minimization of landfilling costs and volume
- CO2 reduction
- Sinter saving up to 5% (BF)
- Short payback period

Similar to the example of recycling of fines in an integrated plant described above, the recycling of fines in an DRI based plants can be applied using cold briquetting technology. In DRI based steel mills there is normally no agglomeration plant such as the sinter plant available which offers the possibility to recycle the generated fine by-products. In many cases it is not economical or generates little added value to sell and transport the materials to other plants for recycling. For these plants, the best recycling concept is to agglomerate the by-products, which reach approximately 10% of mass of the produced DRI capacity, such as dust from the material handling systems, oxide fines, HBI fines and DRI slurry by briquetting with an inorganic binder system. The cold briquetting process itself is similar to the process shown in Figure 2. The produced briquettes are directly fed into the direct reduction plant (e.g. MIDREX) and may replace ferrous materials like iron ore or pellets in the reduction shaft.

2.1 New Developments

The recycling concept for by-products generated in DRI plants is not yet commonly used on a large scale. The great economic value of such a project is determined by the high iron ore and pellet costs, compared to a relatively low operating cost and investment cost for such a plant.

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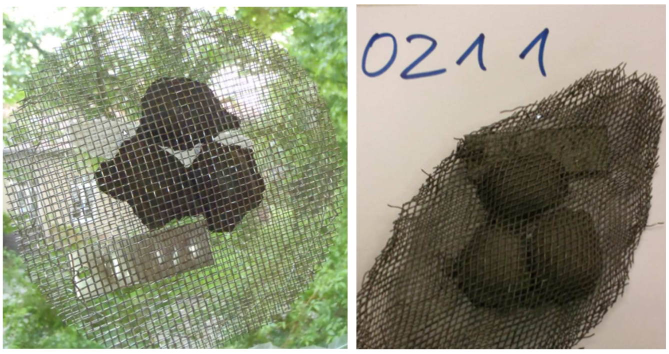
Primetals, based on its experience from similar applications with cold briquetting plants, has invested considerably in laboratory testing to verify the briquetting properties and selection of appropriate binders and process parameters. To verify the right recipe for briquetting such materials and their combinations, several tests on laboratory scale as well as reduction tests simulating gas atmospheres of DRI plants were carried out.
In Figure 5 the oxide briquettes before and after passing the DRI shaft under reduction gas atmosphere are shown. The results fulfill the requirements of a direct reduction shaft concerning the low temperature disintegration (550°C). In Figure 6 the promising results are summarized and compared with iron ore pellets.



(a) before (b) after

Figure 5. Soft basket tests in reduction shaft (a) before test; (b) deformed soft basket after test.

sample no.	test no.	briquette size [cm³]	comp. Strength [N]		shatter strength [%]		basket test results			RDI+6,3mm [%]	porosity [%]
			+0h	+24h	+0h	+24h	executed	metallization [%]	percentage "whole briquettes" [%]		
T02	18624b	10	215	361	96,2	92,1	yes	90	90	76,0	25,3
T10	18624b	10	150	491	97,7	96,5	yes	81	100	77,4	-
T15	18624b	10	338	655	95,3	90,7	yes	87	93	77,8	25,5
T16	18624b	10	194	399	97,2	95,3	no	-	-	76,3	-
T21	18624b	5	185	517	91,5	83,3	no	-	-	80,7	25,8
T06	18665b	5	250	718	84,4	78	yes	94	89	88,0	-
T07	18665b	5	250	670	92,3	82,5	yes	95	100	86,9	27

Figure 6: Summary of test results

These results are promising in the sense that briquettes were produced that are stable under the reduction conditions. The actual basket tests results agreed well with the laboratory tests results, so that conclusion from the laboratory tests can be applied to the actual plant conditions.

3 SLAG VALORIZATION

In a typical integrated steel plant more than 400kg of slag are generated; see **Erro! Fonte de referência não encontrada.** for an overview. Nowadays almost all blast furnace slags are wet granulated and utilized as latent hydraulic agent in the cement industry. For LD (BOF) converter slag, which accounts for about one third of the total slag produced in an integrated steel plant, such stable value-add market and proven technical solution does not exist yet. Conventional ways of utilization of LD slag for

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construction business or fertilizer are becoming less and less economically attractive due to stricter environmental regulations, increasing quality requirements, decreasing market volume and decreasing prices. Furthermore, the typical way of processing of the slag by simple pouring and cooling generates dust emissions, energy loses and requires a serious footprint. An innovative way for modification of the liquid slag for recovery of its metallic content and further utilization of the slag in the cement industry is jointly developed by Loesche and Primetals Technologies. In the cement industry this modified slag is used as cement clinker substitute with a high economic value.

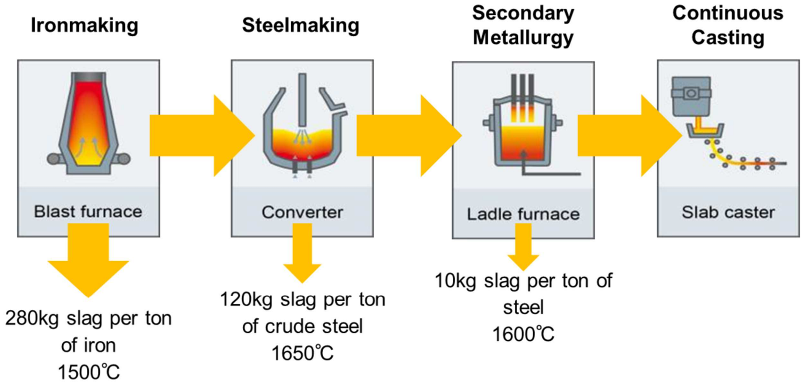

Figure 7. Typical amounts and temperatures of slags in integrated steelmaking, in total more than 400kg of slag are created for each ton of steel casted.

Loesche and its partners discovered that LD slag can be modified in a way that a considerable amount of Alit (C3S) is formed during solidification. The Alit leads to pronounced hydraulic properties of the slag, allowing the use of the slag as cement clinker substitute. The formation of Alit is mainly triggered by the value of the clinker standard (CSt), defined as:

$$95 < \frac{100 \cdot CaO}{2{,}80 \cdot SiO_2 + 1{,}1 \cdot Al_2O_3 + 0{,}7 \cdot Fe_2O_3} < 105.$$

The CSt has to be preferably in a range between 95 and 105 after slag modification to ensure that high mass fractions of Alit are formed. The slag modification itself is done under reducing atmosphere. Coal is injected as reducing agent transforming the iron oxides in the slag back into metals. As a side effect almost all the iron is recovered from the slag due to this modification. The iron recovered can be directly used in its liquid form in the steel plant again, improving the yield of the integrated steel making production route by almost 2%.

Tests with slags from different European steel plants have been performed. The slags were modified, solidified and the materials generated were analyzed in detail.

Table 1. Composition of typical LD slag before and after modification.

	Original LD Slag	Modified Slag
SiO_2	13,9 %	19,6 %
Al_2O_3	1,7 %	2,7 %
Fe_2O_3	28,8 %	2,7 %
CaO	42,7 %	62,3 %
MgO	3,3 %	3,4 %
MnO	5,2 %	3,9 %
P_2O_5	1,1 %	1,1 %
CaO_{free}	4,2 %	2,1 %
CSt	70,1	104,3

From all slags hydraulic active agents with high mass fraction of Alit and good hydraulic properties were generated. Typical slag composition before and after modification is shown in Table 1.
The mass fraction of the main components of typical LD slag before and after modification is given in Figure

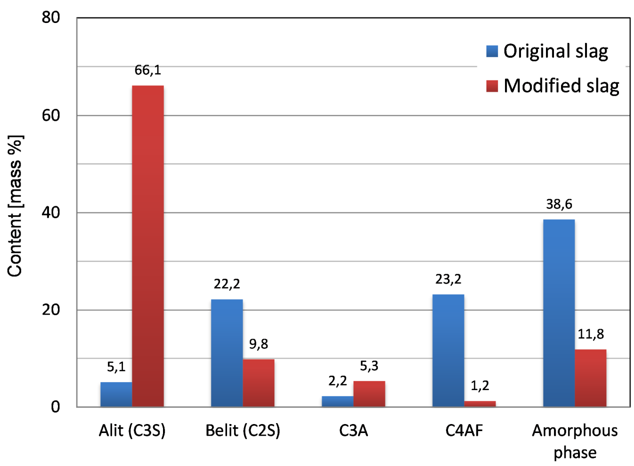

Figure 8. Typical phase distribution for original and modified slag, note the high fraction of Alit. Similar results have been achieved in several other tests with slags from other steel plants.

The figure shows that after modification two thirds of the total mass is Alit, leading to good hydraulic activity and a significant contribution to the compressive strength of mortar, as shown in Figure 9, very left columns. The numbers show that the modified slag contributes to the strength right from the beginning if fine grinding is applied. The final strength after 28 days that is even higher than the strength of the reference mortar made from 100% reference cement.

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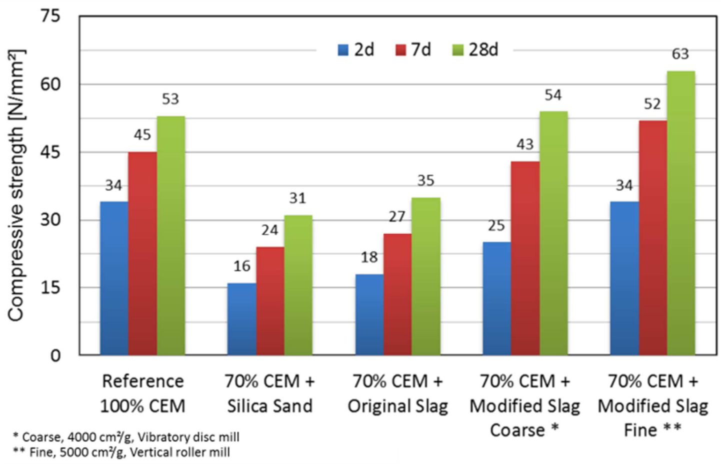

Figure 9. Compressive strength for mortar with reference cement and several mixtures after two, seven and 28 days. Comparison clearly shows that excellent effect of the modified LD slag especially regarding final strength.

The entire process of transforming the liquid slag from the LD process into a substitute for cement clinker is performed in three steps:

1. Modification of the liquid slag and metal recovery
2. Solidification of the slag
3. Grinding and final metal recovery.

For modification of the slag a process similar to Primetals Technologies Zero-Waste Process (ZEWA) is proposed [1]. An aggregate comparable to a ladle furnace could be used for this step; this aggregate allows for continuous slag charging, coal injection and electrical heating. Most of the iron recovered in this step is collected at the bottom of the ladle. The part of the iron that remains in the slag and is tapped with the slag can be almost completely recovered during grinding. Liquid slag needs to be charged to the furnace in order to minimize energy consumption. Of course also solid slag can be added, as it is done e.g. to process skulls. The liquid hot metal at the ladle bottom is not tapped but remains as a hot heel in the ladle. A simplified picture of this process is shown in Figure .

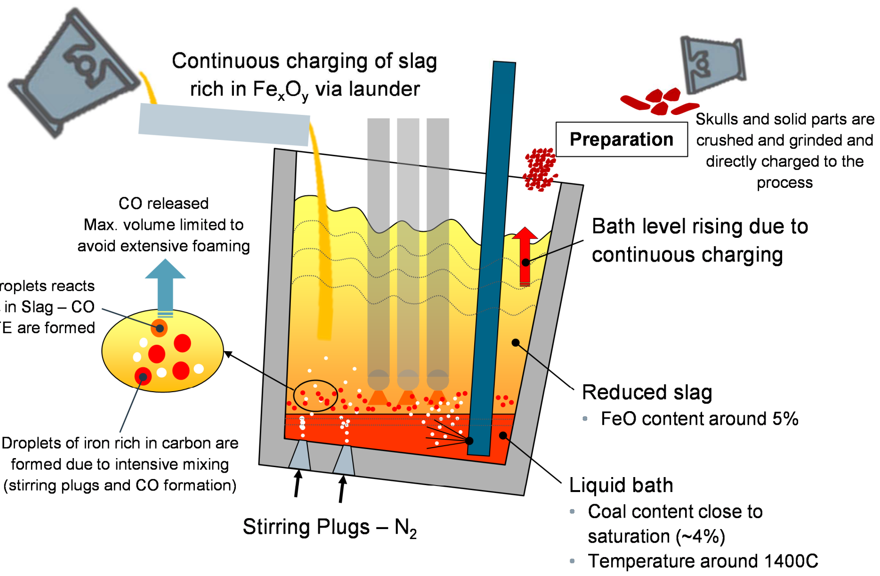

Figure 10. Proposal for process for slag modification in a ladle type aggregate with heating via electrodes and coal injection via lance, slag is continuously charged.

The modified slag needs to be cooled and solidified after tapping. Close temperature control is required within this step until the last phase change temperature is undercut. Equipment solutions for this solidification step are under development, the technical solution applicable strongly depend on the viscosity of the slag after reduction which is expected to be rather high.

For slag solidification, Primetals is in the process of developing a dry slag granulation process with heat recovery, targeting mainly on the granulation of BF slag [2]. For LD slag, Baosteel has developed the BSSF slag granulation technology, which is available worldwide in cooperation between Primetals Technologies and Baosteel Engineering Group. This technology allows direct granulation of liquid slag in a closed granulation drum, avoiding long solidification time and emissions from open pit slag pouring, yielding a granulated slag after short processing times of several minutes. Approximately thirty BSSF units are already in operation and ten under construction, with the majority of plants located in China.

The final step of the process is grinding of the granulated slag and recovery of the remaining iron in a Loesche Vertical Roller Mill.

4 CONCLUSION

Many iron and steel plants already practice recycling of by-products to a certain extent, however there is still room for increasing the value creation by optimizing the recycling concept and finding new innovative applications. One of these applications is recycling of by-products in DRI plants by cold briquetting and using the briquettes as iron ore or pellet substitute. A similar concept is used in integrated plants by cold briquetting of by-product fines and recycling the briquettes in blast furnaces and BOF converter plants.

For the valorization and better utilization of LD slag the transformation into a valuable product and in the same step recovering its metallic content is the target of the process which is currently developed by Loesche and Primetals Technologies. Numerous laboratory tests with slag from different plants have shown that a hydraulic highly active component can be generated in a reproducible manner. More detailed investigations of the mechanisms behind and trials how such process can be realized in full industrial scale are running. Economic considerations prove the economic potential of the process and show that earnings from cement clinker substitute and iron recovered are of equal importance.

5 ABBREVIATIONS

LD	Linz Donawitz (BOF) process
DRI	direct reduced iron
HBI	hot briquetted iron
RDI	reduction degradation index
BSSF	Baosteel Slag Short Flow

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