DE-OILING OF OILY MILL SLUDGE AND SCALES[1]

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Abstract

With ever increasing environmental legislations, shortages of raw material supply and high metal prices, the implementation of dedicated processes for treating metallurgical residues and recovering their valuable contents becomes more and more relevant. Oily mill sludge and scales are part of these residues. Their internal recycling in Sinter Plants, BF's or BOF's are more and more restricted due to off-gas emissions, increasing risk of ESP explosion, abrasion issues, and their impact on steel quality. Paul Wurth, an Engineering and Technology supplier for the Iron and Steel industry, and Lhoist, a leading producer of calcium oxide and magnesium oxide based chemicals, developed an innovative auto-thermal process PLD (Paul Wurth Lhoist De-oiling), which is based on a low temperature pyro-metallurgical approach by using lime, thus providing an efficient and economical solution to steelmakers.

In this process, a combination of exothermal chemical reactions and a controlled oxidation process destroys the hydrocarbons contained in the oily sludge and the recovery of the premium iron ore is ready to be re-used in the Sinter Plant. Thanks to an appropriate off-gas cleaning system, exhaust gases are treated so as to limit gas emissions in terms of VOC, CO, PCB, PAH, SO_2, PCDDs, PCDFs, etc…This paper will describe the PLD process efficiency by presenting results of semi- industrial tests and economic benefits

Keywords: De-oiling; Oil; Sludge; Scales; Hydrocarbons; Auto-thermal.

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1 INTRODUCTION

All over the world the Steelmaking industry has to comply with more and more stringent environmental regulations. Gas, liquid, solid wastes and effluents have to be captured and stabilized, and if possible further processed for their content in valuable metals. One such by-product is the oily sludge and scales produced from the hot rolling mill process.

For a long time, dumping of high oily by-products (above 1% of hydrocarbons) in waste disposal sites was the most common way to get rid of such residues. Therefore, in the last decade, steelmakers were faced with increasing stringent environmental laws and the rise of raw materials prices. Then, to limit their amount and recycle them to value its iron content and energy capacity becomes more and more relevant. Existing different ways for recycling such by-products consist of:

- Internal recycling in the Iron and Steel making process
- External recycling via a dedicated treatment and then recycle the de-oiled product in the main process as iron ore
- Selling it to other industries such as cement plants

Even if such recycling processes avoid the dumping of oily by-products, they will never efficiently combine both environmental and economic benefits. Internal recycling through main processes like Sinter Plants, Blast Furnace, Converters or Electric Arc Furnaces leads to several constraints such as: charge preparation (e.g. briquetting), environmental issues (VOC deflagration in electro precipitators and dioxin emissions) and main process problems. Regarding external recycling, the main treatments consist in either pyrolysis of oil but it requires high fuel consumption, or washing using surfactant but its efficiency is limited mainly due to the fine grain size of sludge. By-product selling to other industries usually generates small profits due to the low valorisation of iron content and the limited amount of demand.

Therefore, the respective metallurgical and chemical expertise of Paul Wurth and Lhoist led to the development of a low temperature process using lime, named PLD process, thus providing an efficient, flexible, compact and economical solution to steelmakers. The process was patented in 2008 (PCT Pub. No.: WO2008/037703).

This document is intended to introduce the PLD technology for de-oiling oily sludge and scales in an environmental way and present its economic benefits.

2 PRINCIPLE

The principle of the PLD process is to treat oily by-products produced by hot rolling mills via an auto-thermal and “zero-waste” process using lime and recover valuable de-oiled products which can be recycled in a Sinter Plant as a substitute for raw iron ore.

The Paul Wurth Lhoist De-oiling process is based on a close mixing of the oily by-products together with specific quicklime inside a Multiple Hearth Furnace (MHF).

Thanks to a specially designed low temperature MHF and a controlled mixing, lime reacts with water contained in the residue, inducing a quick temperature rise, followed by a 45-minute complete oxidation of the organic compounds (at a temperature below 500 °C), leading to CO_2 and H_2O as end-products. Then, high energy efficiency transfer of the furnace and a controlled oxidation of organic volatiles enable it to make the process auto-thermal. Fuel gas is only used to maintain equipment hot during shut-down periods.

The recovered product is completely de-oiled (residual oil[1] below 0,1%) and is mainly composed of iron oxide (85~90%) mixed with calcium based compounds

(5~10%). The PLD product can easily be recovered as, for example, raw iron ore on the Sinter Strand in order to value its iron content.
A PLD plant is equipped with an off-gas cleaning system enabling it to treat emissions containing volatile organic compounds, carbon monoxide, dioxins and dust emissions. Therefore, an off-gas cleaning system could be adapted so as to achieve more severe emissions.
Conceptual process flow sheet of PLD process is shown in the Figure 1:

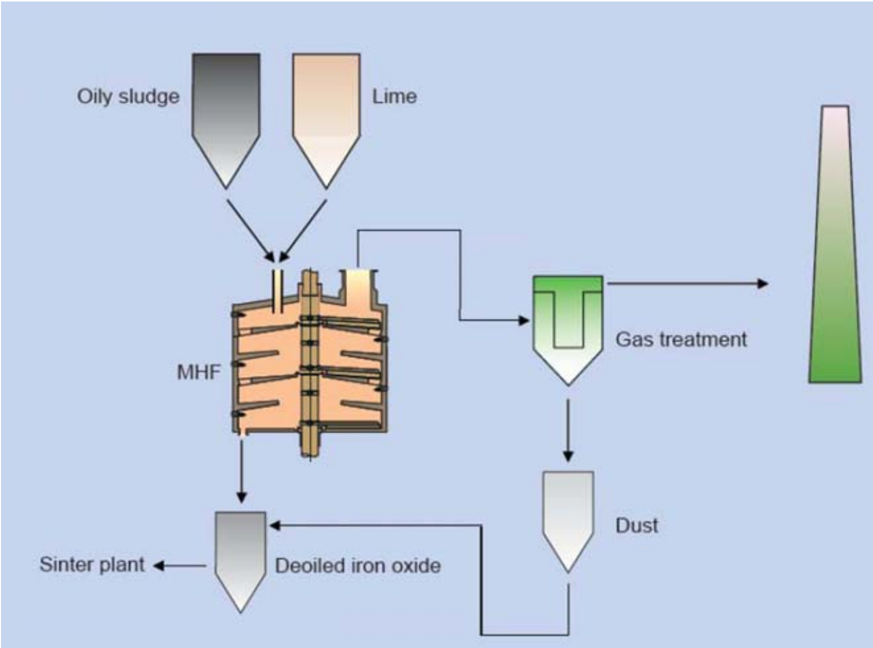

Figure 1: Conceptual process flow sheet of PLD process

3 MAIN PROCESS FEATURES

Mainly due to the design of the Reactor and low temperature processes using lime some features and advantages in comparison with others technologies are highlighted here below:

- Flexible operation. A plant could be started and stopped in a limited time period, which offers the operator to manage its PLD plant production in a flexible way, for example by stopping the PLD plant during weekends
- Using lime enables to limit SO_2 emissions produced by sulphur contained in lubricating oil
- Stable operating conditions due to individual control of temperatures zones in the furnace and an efficient mixing between raw materials and lime
- Efficient reactor in terms of energy transfer between process gas and burden
- Efficient de-oiling performance independent of raw materials grain size
- Low energy consumption, by using oil contained in raw materials as fuel for process. This feature makes, most of the time, a PLD process as an auto-thermal process (no need of external fuel energy during operation) and a thermal process reducing greenhouse emissions
- "Zero waste" process. No effluent or residues are produced by a PLD process

Typical mass balance of PLD technology processing 1 ton of oily sludge polluted with 20% of moisture and 7% of oil (dry basis) is presented as follows:

[1] *Oil assumed as Total Organic Carbon and measured with norm DIN-13137*

- Inputs:
  - 1 ton of oily sludge
  - 50 kg of quicklime
  - < 5 Nm^3 of natural gas
  - 0,8 m^3 of water
- Outputs:
  - 740 kg of de-oiled product
  - 2.500 Nm^3/h of process off-gas

Typical emissions are listed here below:

- No effluent by using dry quenching of process off-gas
- Guaranteed off-gas emissions at stack:
  - Dust < 20 mg/Nm^3_{dry}
  - TOC < 50 mg/Nm^3_{dry}
  - SO_2 < 350 mg/Nm^3_{dry}
  - NO_x < 350 mg/Nm^3_{dry}
  - PCDD/DF < 0,1 mg/Nm^3_{dry}

Nevertheless, in order to comply with ever increasing emission regulations, the off-gas system can be adapted.

4 TESTING RESULTS AND STATUS OF PLD TECHNOLOGY

4.1 Testing Results

Research activity regarding the PLD process began in 2006 by performing preliminary tests with a batch of 10 kg. These tests proved the efficiency of the PLD process to de-oil more than 10 different oily sludges and scales produced by European integrated and mini mills. In order to prove the PLD efficiency and set the concept of an industrial plant, two (2) continuous tests were performed. The main results of the semi industrial tests are presented here below:

- Continuous testing condition n°1:
  - Duration: 8 hours continuously
  - Material treated: 400 kg at 50 kg/h
  - Treated oily sludge: 6% of oil ; 14% of moisture
  - Lime consumption: 40 kg at 5 kg/h
  - Operating temperature: 300 – 430 °C
  - Residual oil in product: < 0,1%
  - Residence time: 60 minutes
- Continuous testing condition n°2:
  - Duration: 96 hours continuously
  - Material treated: 10 tons at 100 kg/h
  - Treated oily sludge: 18~20% of oil ; 20% of moisture
  - Treated oily scales: 1% of oil ; 2~10% of moisture
  - Residence time: 60 minutes

  Pilot plant was composed of:
  - Charging unit enabling to feed the furnace up to 100 kg/h (nominal charging rate during testing)
  - Refractory lined multiple hearth furnace composed of 5 self-supporting hearths
  - Discharging water cooled screw

- Off-gas cleaning system composed of a Cyclone, Post Combustion Chamber, Scrubber, Fan and Stack equipped with on-line off-gas monitoring (temperature, emissions, etc…)

The different tests and results are presented in the table hereafter:

Trial #	TOC in feed % (wet basis)	CaO amount % of wet feed	Furnace temperature °C	Residual TOC in final product % (dry basis)
1	**8**	**5**	**500**	**< 0,1**
2	**4**	**5**	**440**	**< 0,1**
3	**2**	**5**	**380**	**< 0,1**
4	**10**	**5**	**410**	**0,2**
5	**4**	**0**	**300**	**0.2 ~ 0,4**
6	**4**	**5**	**300**	**0,1**
7	**4**	**10**	**300**	**< 0,1**

ns

Oily sludge PLD product

Figure 2: Oily sludge (8%TOC 19%H_2O) and PLD product (Residual TOC < 0,1%)

TOC analyses on final products clearly show the efficiency of the PLD process for de-oiling high and low oily materials. Nevertheless, some residual organic compounds were measured in the final product of test #4. The process could be improved by adjusting the temperature profile of the furnace and increasing the lime amount up to 10%. Regarding the lime impact on process, tests #5-6-7 showed the benefits at low temperature.

Furnace temperature during testing is presented hereafter:

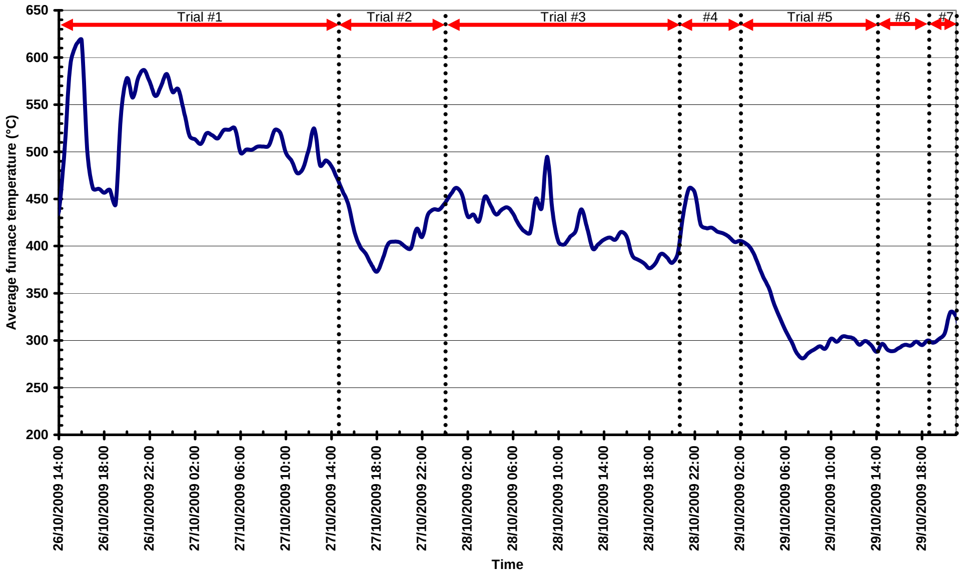

Figure 3: Furnace temperature during continuous PLD testing.

Testing started with a high furnace temperature (500~550°C), mainly due to uncontrolled air intakes in the pilot furnace. Further trials were performed at lower temperatures (from 450°C down to 300°C) and were controlled accurately by means of air injectors. All trials have been performed without any additional energy supply (burners switched off), proving that the process enables it to auto-thermally de-oil the sludge which contains more than 3% of organic compounds.

Continuous emission monitoring for carbon dioxide (CO_2), oxygen (O_2), sulphur dioxide (SO_2), oxides of nitrogen (NO_x), carbon monoxide (CO) and volatile organic compounds (VOC) was conducted at the after-burner (post-combustion chamber) exhaust.

Following table presents main results of off-gas monitoring:

Table 1: Summary of off-gas measurements

Gas data	PCC off-gas
Temperature (°C)	**> 700°C**
O_2 (%vol dry)	**> 4%**
CO (%vol dry)	**< 50 ppm**
VOC (%vol dry as CH_4)	**< 50 ppm**
NO_x (%vol dry)	**< 50 ppm**
SO_2 (%vol dry)	**< 1 ppm**

These results point out that low operating temperatures combined with an efficient post-combustion can achieve lower emission limits.

4.2 Status of Technology

The PLD process efficiency in semi industrial conditions has been achieved and demonstrated. Therefore a PLD plant is ready to be commercialized and be adapted according to a client's requirements. Moreover, so as to start developing such technologies, Paul Wurth and Lhoist R&D have applied jointly for European subsides for the erection of the first PLD plant in Europe.

5 PLD PRODUCT

Typical chemical analysis of PLD product is presented here after:

Table 3: Typical PLD product chemical analysis

H2O (%)	TOC (%dry)	Fe (%dry)	O (Fe_xO_y) (%dry)	CaO (%dry)	S (%dry)	Gangue (%dry)
< 0,1	**< 0,1**	**~65**	**~23**	**5~10**	**~0,05**	**balance**

Grain sized PLD products highly depend upon the initial grain size of the oily by-products. In order to facilitate its handling and avoid further dust emissions during its handling, some humidification of the PLD products or other kinds of preparation such as micro-pelletizing, pelletizing or briquetting could be achieved.

6 INDUSTRIAL PLD PLANT

6.1 Layout and Footprint

A typical layout of a PLD plant is quite compact, as presented here below:

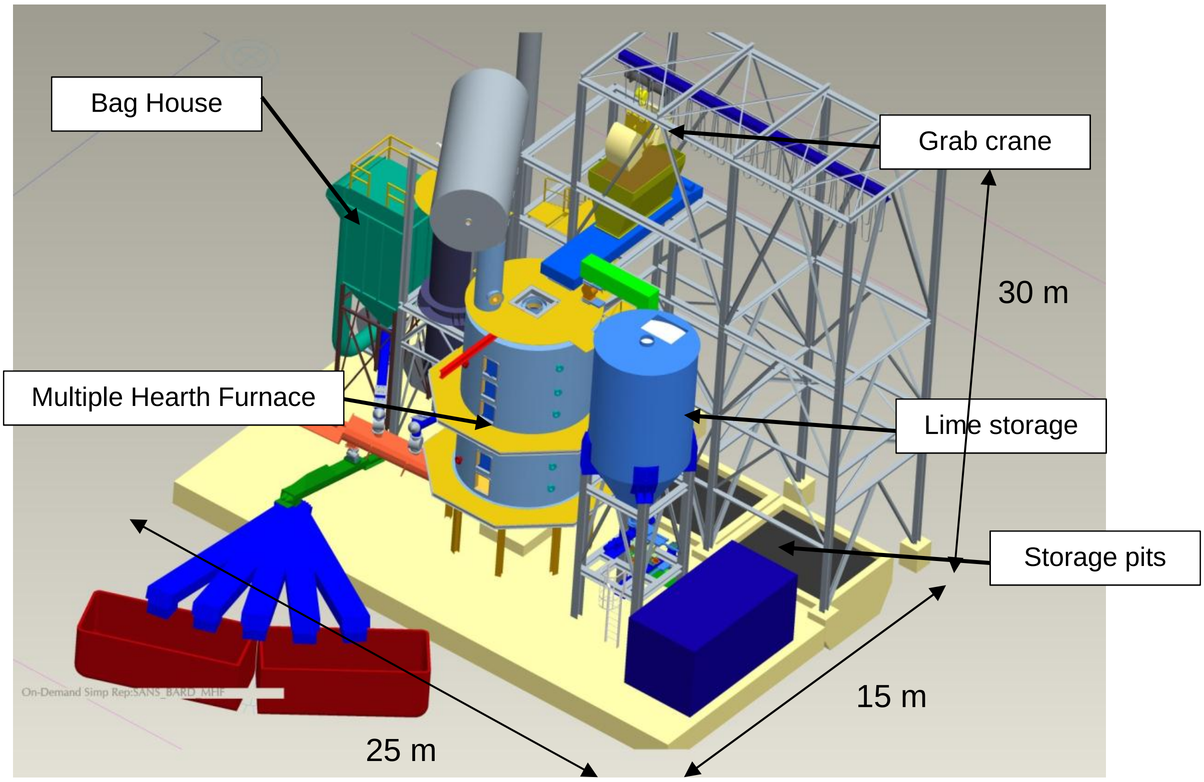

Figure 4: PLD plant 3D layout

6.2 Key Characteristics

- Plant capacity: 25.000 to 100.000 tons per year
- Availability: > 95%
- Sludge throughput: 3 to 13 tons per hour
- MHF inner diameter: 3,5 to 5 m

7 ECONOMICS

Regarding the investment cost, the total investment for a PLD plant is in the range of 7 to 9 million Euros, depending on the yearly amount of residues and on the total amount of organic compounds to treat per year. In fact, material handling and the furnace itself mainly depend on the total amount of residues, whereas the size of the off-gas cleaning system depends on the hydrocarbon content in feed.
Regarding operating costs, they are in the range of 20 to 30 Euros per ton of wet residue, mainly depending on the lime input used for the process.
As to the credits, PLD process:

- Produces a pure iron source which can be considered as high grade iron ore. Its estimated value is about ~80 Euros per ton of de-oiled product
- Saves dumping costs (about 70 Euros per ton of oily by-product in Western Europe) and when integrated into a steelmaking plant the transport costs of the oily residues

Economics profitability depending on yearly amount of oily sludge is presented in the Figure 5:

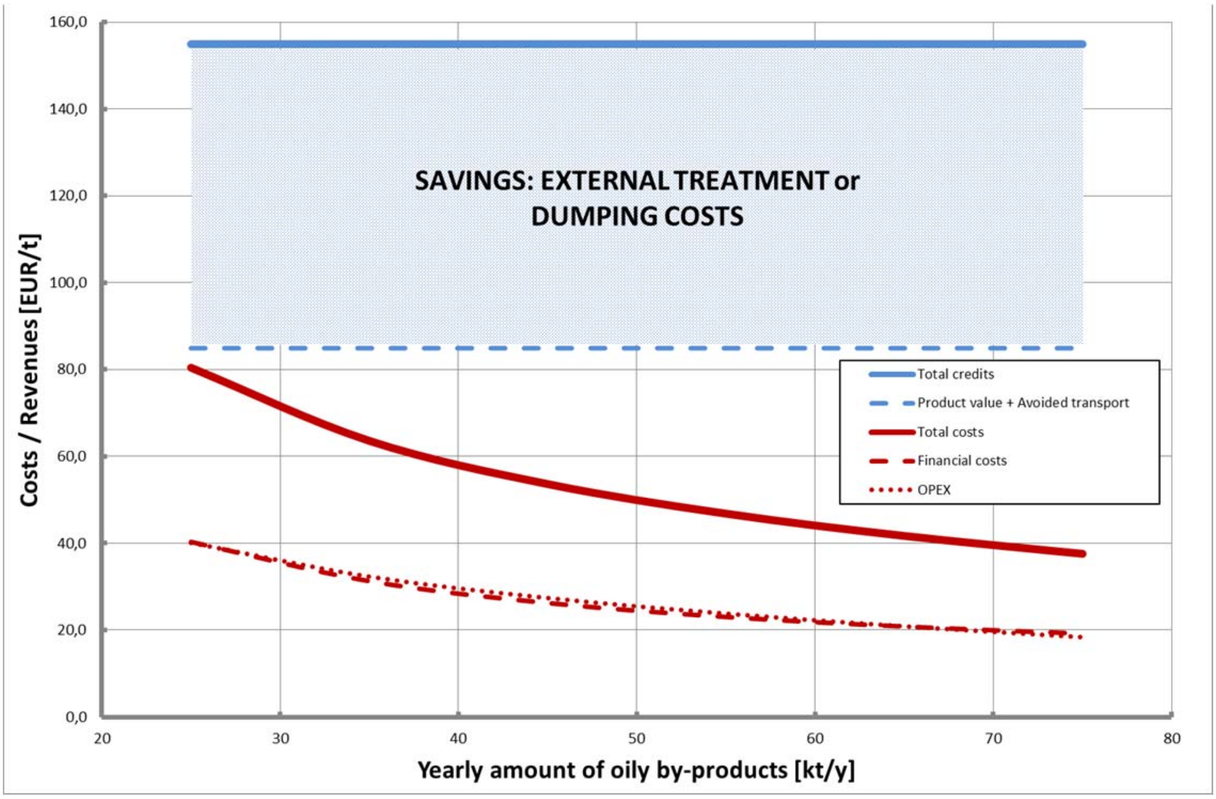

Figure 5: PLD economics profitability

6 CONCLUSION

The recycling of oily by-products generated by a rolling mill process is a priority for most steelmakers, not only due to the stringent environmental legislation, but also to the high cost of “virgin” raw materials. Thus, in the near future, “zero waste” recycling technologies will be a key point for the sustainability of metallurgical operations. The PLD technology presented in this paper achieves this environmental challenge and an economical one as well. Indeed, it even has a positive impact on the performances of steelmaking and in most cases repays the investment cost within 3~4 years.

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