特集記事●8
地球環境を考慮した排出ガス削減への鉄鋼業の取り組み

Steel Plants Are Greener Than You Might Think

環境対応が進む製鉄プラント

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Abstract:

Ever stricter regulations by governmental institutions require lowest emission levels for existing and greenfield iron and steelmaking plants.

The dry gas cleaning technology (MEROS®) reduces the emissions of SO_2, heavy metals and dioxins from sinter plants safely below the required emission levels. Such low emission levels are maintained by a multi-component additive injection upstream of a high-performance fabric filter, while the installation of a (selective) waste recirculation technology minimizes the investment cost for the gas treatment.

Residues and by-products arising from the gas treatment are often disposed, leading to consumption of valuable landfilling volume and high cost as such material has to be stored under special conditions to avoid uncontrolled leaching of salts and heavy metals.

The innovative leaching process is closely linked to the MEROS plant and minimizes on site the residue volume. After dissolving of the residue a series of treatments steps of the waste water ensure the compliance with the most stringent discharge emission limits prior to the release of the clean brine into the sea. The proposed solutions can be applied to existing and greenfield plants.

要旨

製鉄、製鋼プラントからの排出ガスの規制レベルがこれまで以上に厳しくなっている。

本紙で紹介する乾式ガス浄化技術（MEROS®）は、焼結プラントから排出されるSO_2、重金属、ダイオキシンを、高性能ファブリックフィルターの上流に多成分添加剤を注入することで必要排出レベルまで低減でき、更に廃棄物を再循環処理することで、ガス処理コストを低減できる。

一方、排出ガス処理時に発生する残留物、副産物は、塩や重金属流出防止処理をして埋め立てするためコストが掛かる。MEROSに搭載されるリーチングプロセスは、その残留物量を最小限に抑え、処理後廃水も厳しい排出規制をクリアできる革新的な技術である。この技術は既設、新設どちらにも適用できる。

1 Introduction

Irrespective of the ongoing climate change, other emissions arising from steel production harm human populations as well. In 2014, 90% of the world's population of urban areas were exposed to fine particulate matter concentrations exceeding the World Health Organization (WHO) Air Quality Guidelines. The consequence is an increasing risk for non-communicable diseases[1]. To reduce the risk for the population, governmental institutions apply stricter environmental regulations. These new regulations require lower emission levels for iron- and steelmaking

Table1 Emission figures acc. BAT[1).]

Emission Figure	Sinter Plants	Blast Furnace	BOF Prim.	BOF – Sec.
Dust Emissions [mg/Nm³]	Bag Filter: < 10 ESP: < 30	Bag Filter: < 10 WDS: < 10	DDS: < 20 WDS: < 50	Bag Filter: < 10 ESP: < 20
Capture Efficiency [%]	n.a.	n.a.	n.a	> 90
Hg [mg/Nm³]	< 0,03-0,05	n.a.		
SOx [mg/Nm³]	< 350	< 200		
NOx [mg/Nm³]	< 250	< 100		
PCDD/PCDF [ng-I-TEQ/Nm³]	< 0,05-0,2	n.a.		

plants.

Besides new installations, also existing gas cleaning systems have to comply with the most stringent environmental regulations set by national and local governments. Especially for existing sinter plants the modernization and revamp of their off-gas systems is a challenge to achieve the future emission standards.

The European BAT document provides an overview of emission figures which have to be typically achieved by European steel plant operators. Table 1 gives an overview of the main emission figures summarized in the conclusions of the BAT document.

The later described gas cleaning solutions for sinter plants clearly complies with all those required values.

In addition to gaseous and solid emissions from steel plants, the demand for increasing energy efficiency and CO_2 reduction is one of the global megatrends of our time. The upgrade of existing ironmaking facilities with energy efficiency systems supports sinter plant operators to cut their operational costs and reduce their carbon footprint.

In the following sections a comprehensive environmental solution for sinter plants considering gaseous and particulate emissions as well as solid residuals and increasing energy efficiency is described.

2 Maximized Emission Reduction for Sinter Plants (MEROS)

More and more, the design and operation of sintering plants have to address various environmental aspects. To meet these challenges, Primetals Technologies developed MEROS, an innovative technology to reduce harmful emissions from sintering plants.

Fig.1 MEROS plants at voestalpine (Austria) and Masteel (China).

Thanks to the MEROS process, up to 99% of harmful and toxic components such as fine dust (PM10; PM2.5), dioxins (PCDD/F), volatile organic components (VOC) and heavy metals (e.g., Hg, Pb, Cd) can be removed from waste gas. Acidic gases, such as hydrogen chloride (HCl), hydrogen fluoride (HF) and sulphur dioxide (SO_2) – are removed to levels previously unattained with conventional gas-treatment techniques. With an additional DeNOx module, based on SCR (Selective Catalytic Reduction) technology also nitrogen oxides (NOx) are removed below required values.

2.1 General process description

The MEROS process is characterized by a series of treatment steps in which dust and pollutants still present in the sinter off-gas after the electrostatic precipitator are further reduced. This process uses adsorbents such as specially prepared lignite coke or activated carbon and desulfurization agents like hydrated lime or sodium bicarbonate as additives which are injected into the sinter off-gas stream. High relative velocities (particles vs. sinter gas) in combination with a homogeneous injection of the additives are essential for a fast reaction and high conversion rate of the additives.

The injection of specific desulfurization agents into the off-gas stream promotes DeSOx reactions as well as reactions with other acid gases, e.g., HCl. Approximately 50% of the gas-cleaning activities in the MEROS process already take place during the adsorbent-injection step. With its highly porous structure, the carbon adsorbent physically binds the heavy metals and organic complexes like VOCs, and dioxins/furans.

Depending on the local requirements and conditions, two principal processes have been designed based on different desulphurization agents - either sodium bicarbonate or hydrated lime.

MEROS process based on Sodium Bi-Carbonate (SBC)

The Primetals Technologies patented MEROS process is a highly efficient dry gas cleaning process, latest state of the art. The technology is based on the following process steps (flow sheet shown below):

- Milling of SBC to very fine powder
- Injection of SBC upstream of bag filter
- Recirculation of dust
- High Performance Pulse jet bag filter

Sodium Bicarbonate (SBC) is injected into flue gas and reacts with acid components (e.g. SOx) in the flue gas, which minimize the risk of acid corrosion for any equipment or duct after the injection point. The reaction products and other emissions are captured at the bag filter and major share of this by-product is recirculated to flue gas in order to optimize the utilization rate of the injected additives. Part of the by-product is discharged to the storage system.

Main objective of SBC injection is the desulfurization of the off-gas (DeSOx). As an additional benefit, the reduction of heavy metals, PCDD/F (Dioxins/Furans) and other toxic organic compounds VOC (volatile organic compounds) can be achieved by injecting additional additives, such as activated carbon or lignite.

The acid neutralization using sodium bicarbonate involves in fact a stage of thermal activation: brought into contact with the hot flue gases (>80°C is required), the sodium bicarbonate converts rapidly into sodium carbonate, with an extremely high specific inner surface and porosity.

The conversion of the sodium bicarbonate into 'activated carbonate' makes that material an excellent way of neutralizing acids (hydrochloric acid, sulfur dioxide, hydrofluoric acid, etc.) and by injecting of an additional additive (e.g. activated carbon) which focuses on adsorbing the heavy metals, dioxins and furans. Typical performances

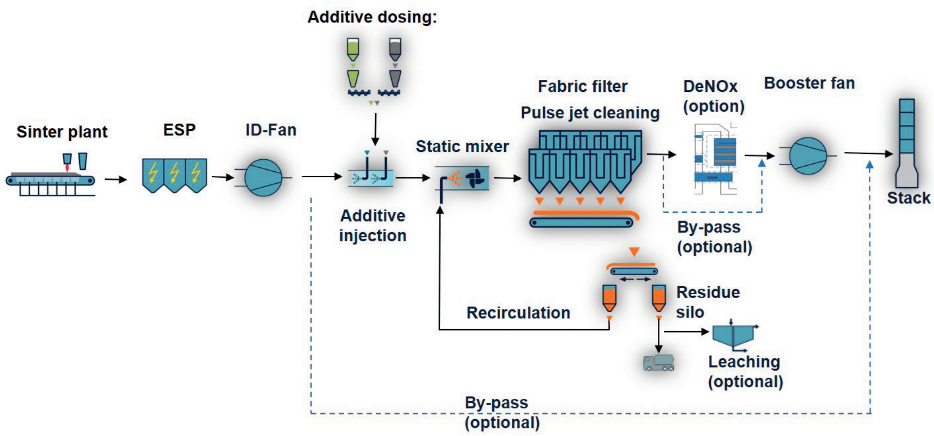

Fig.2　Flow sheet of MEROS process based on sodium bicarbonate.

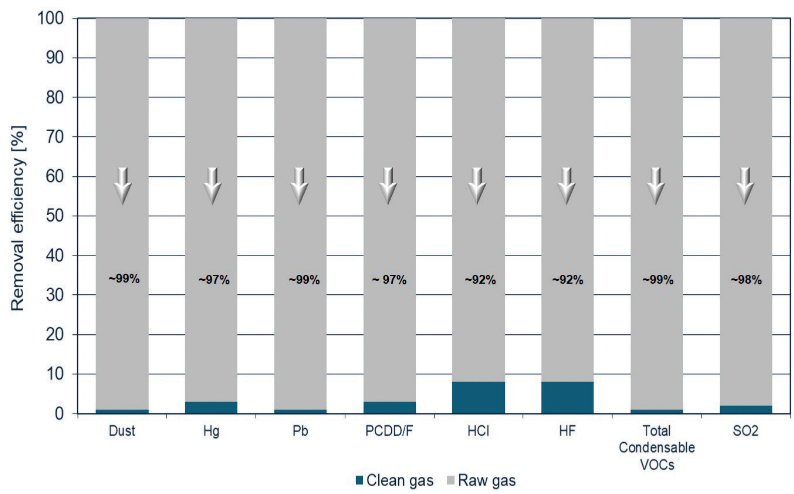

Fig.3　Typical performance of MEROS process.

are shown in Fig.3.

A pulse jet (fabric) filter is used to capture the reaction products that are generated during the DeSOx process together with the dust in the flue gas. Most of the dust separated by the pulse jet filter is recirculated back to the waste-gas stream just in front of the pulse jet filter. Doing so, the still unreacted parts of sodium carbonate as well as unutilized adsorbents are once again contacted with the waste gas and the effective usage rate is essentially increased. Such operation results in a minimized operation cost figure.

In case also NOx concentration has to be decreased, a DeNOx step is required downstream of the fabric filter. The lower the remaining SOx level the lower can be the SCR catalyst operation temperature, and since there is almost no temperature drop of MEROS-SBC, , the re-heating fuel consumption is less compared to hydrated lime DeSOx, thus resulting in remarkably reduced operation cost .

Fig.4 MEROS plants at a Turkish steel plant for three sinter machines.

The key advantages of SBC DeSOx are:

- Reliable DeSOx efficiency up to 98%;
- Utilization efficiency (stoichiometry) close to 1 resulting in less by-product;
- Completely dry process – no water consumption, no sticking;
- No temperature drop - less energy and investment costs for reheating for the SCR DeNOx step;
- No reactor tower for conditioning required
- Simple process - lower investment costs, minimum maintenance required.

The MEROS process based on SBC was recently installed for three sinter plants at a Turkish steel making facility. The modernization of the waste-gas system for all three sinter plants was realized in less than one year.

The complete overview of the MEROS plants for all three sinter plants is given in the next Figure.

Further SBC MEROS installations are actually being realized in Japan at JFE Fukuyama sinter plant #3 and at two sinter machines for Arcelor Mittal Italy at Taranto works (4 MEROS lines).

At JFE Fukuyama Sinterplant No.3 a MEROS system will be installed downstream the newly erected sinter plant. DeSOx removal is designed to achieve more than 97% SOx removal with sodium bicarbonate and dioxin removal to below 0,1 ng(I-TEQ)/Nm^3 using activated carbon as additive.

MEROS process based on Hydrated Lime (HL)

The moisturized HL particles react with all acid gas components in the sinter waste-gas to form reaction

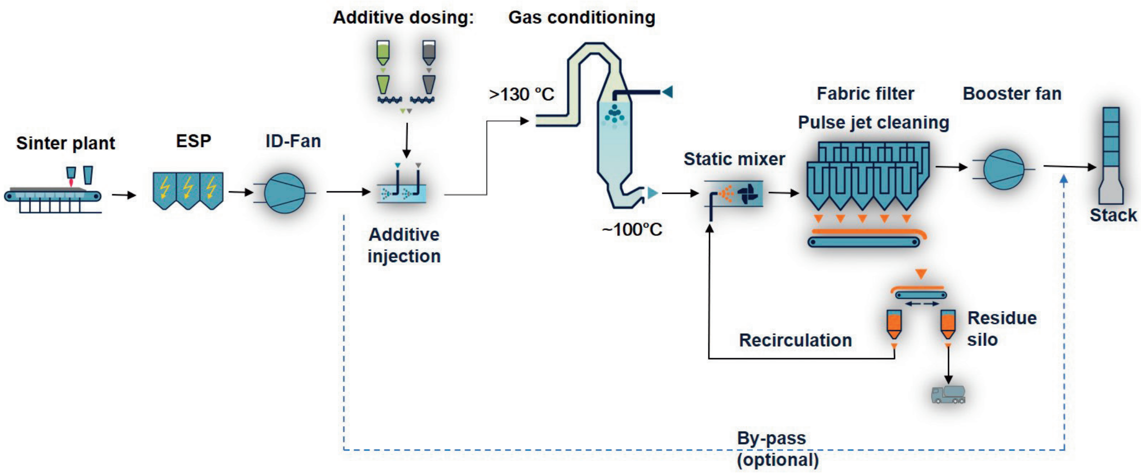

Fig.5 MEROS process based on hydrated lime.

products. It was verified that different HL products show major differences in efficiency for desulphurization. DeSOx rates up to 90% can be maintained applying HL.

Comparison of MEROS SBC vs. HL

The use of SBC is preferred if highest DeSOx rates (>85%) and/or a SCR DeNOx module are required (or expected in future) or where land-filling costs are specifically high respectively not possible.

Fig.6 explains the difference of the reaction behaviour between both DeSOx additives. Extremely fast kinetic reaction of SBC for DeSOx applications allows controlling the clean gas emissions by set-point operation. Concentration peaks of SOx in the raw gas do not impact the targeted concentration of SOx in the clean gas. In comparison HL reaction kinetics is much slower. Any quick change in SOx concentration in the raw gas is directly followed by the clean gas concentration. If a higher DeSOx degree is required the system needs a certain stabilization time. The stoichiometry (depending on the HL quality) is usually in the range of 1.5-1.8.

Heavy metals and organic compounds thereof with low vapour pressure, like mercury salts, cadmium or lead, are removed as particulates at the filter bags. Since the remaining clean gas dust content is extremely low (less than 5 mg/Nm^3), these parts of heavy metals easily comply

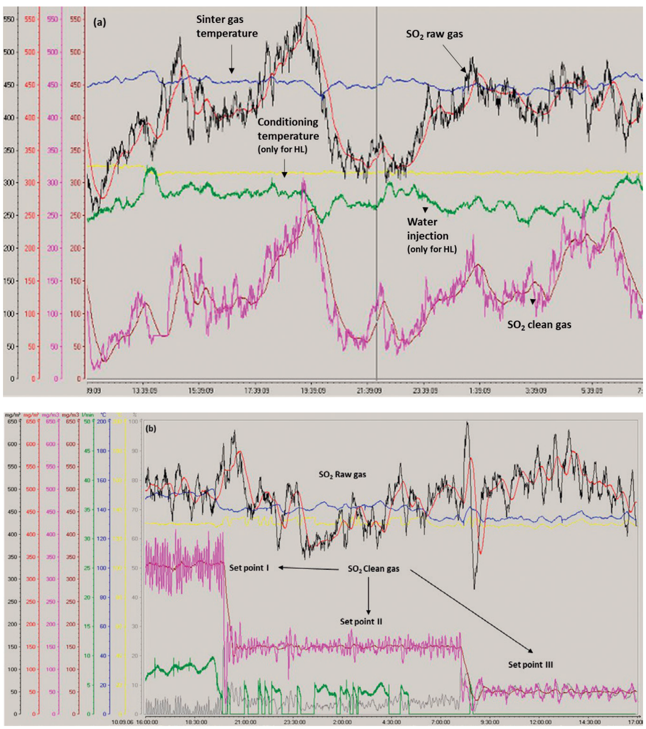

Fig.6　Typical DeSOx curve using (a) hydrated lime or (b) sodium bicarbonate.

with all current global regulations. The gaseous portion of those pollutants and metallic mercury, which have a high vapour pressure, is removed by adsorption at lignite coke or activated carbon. Organic compounds such as dioxins and furans (PCDD/F) and total condensable VOCs are eliminated by more than 99 percent.

Table3 gives an overview of the recent installations and of projects under execution and construction of the MEROS technology for sinter plants.

Table2　Comparison of SBC and HL for DeSOx application.

	Sodium bicarbonate (SBC)	Hydrated lime (HL)
DeSOx efficiency	> 95% depending on injection rate	up to 85% depending on injection rate and reactor temperature
Stoichiometric factor	1,05 – 1,2	1,5 – 1,9
Residual amount	~ 70%	100%
Reagent costs	150-200%	100%
Exit-gas temperature	equals inlet temperature	85 - 100°C
DeNOx (if required)	~ 70% gas for reheating to 270°C	100% gas for reheating to 270°C

Table3　Reference installations of the MEROS technology System.

Reference	Gas Flow [Nm³/h]	Additive
voestalpine Linz, Austria: 2005	650.000	Hydrated lime / Sodium bicarbonate, Activated Carbon
Maanshan Iron & Steel Co.Ltd: 2009	520.000	Hydrated Lime
Kardemir Iron Steel Industry Trade & Company Inc: 2018	SP3: 400.000	Sodium Bicarbonate
Kardemir Iron Steel Industry Trade & Company Inc: 2019	SP1, 2: each 400.000	Sodium Bicarbonate
JSW Steel Ltd.: under construction	SP4: 430.000	Limestone / Hydrated Lime
JFE Steel Corporation: under construction	SP3	Sodium Bicarbonate, Activated Carbon
ArcelorMittal Italia: under execution	SP1, SP2: each 2x 815.000	Sodium Bicarbonate, Activated Carbon
Metinvest - EMZ, Ukraine; on hold	570.000	Sodium Bicarbonate, Activated Carbon

3 (Selective) Waste Gas Recirculation ((S)WGR) System

The (Selective) Waste Gas Recirculation ((S)WGR) system had been developed by Primetals Technologies more than a decade back. It has been proven by several reference plants worldwide that sinter production costs are significantly reduced by applying (S)WGR and also the size of downstream waste gas cleaning system (MEROS) can be reduced leading to much lower investment costs.

3.1 Process description

The air sucked through the sintering bed provides the oxygen required for the combustion of the fuel added to the raw mix and accelerates the flame front through the sinter bed. This air volume is considerably higher than required for the complete combustion of the fuel in order to allow a high velocity of the flame front. Sinter waste gas therefore typically contains approximately 12–13 Vol% residual oxygen concentration, which is sufficient for recirculation to the sintering process after the addition of a small amount of supplementary air. A part of the waste gas is recirculated to a recirculation hood which covers a part of the sinter strand.

Primetals Technologies offers three different waste gas recirculation processes. An overview of the different processes is shown in Table 4.

One of the possible recirculation modes is the so called Waste Gas Recirculation (WGR). Here a part of the waste gas is taken after the waste gas fans and is recirculated back to the sinter strand. This mode does not allow to select the waste gas from individual wind boxes, thus it is non-selective.

The other two possible recirculation modes are selective, therefore also called Selective Waste Gas Recirculation (SWGR). For Selective Waste Gas Recirculation processes the recirculation gas is taken only from selected wind boxes. The length of the suction area including all wind boxes typically can be split into three sections. For recirculation the second section (see Fig.7) or the first and the third sections (see Fig.8) can be used. The recirculated gas has to be pre-cleaned in cyclones or Electrostatic Precipitators (ESPs) to protect the recirculation fan from wear and sinter bed from tightening with dust particles. The part of the waste gas which is not recirculated is transported to a waste gas cleaning unit (cyclones or ESPs and additionally desulphurization (DeSOx) or denitrification (DeNOx) plant) for minimizing the gaseous emissions and emitted to the atmosphere via a waste gas stack[1].

The characteristic distribution profiles along the sinter strand for waste gas temperature as well as waste gas components, such as CO, CO_2, SO_2, O_2, NOx and dioxins are decisive for the design of the SWGR system. Fig.9 to Fig.11 show dimensionless, normalized distribution curves for the main waste gas components and waste gas temperature along the length of the sinter strand. It has high importance for the chemical composition of the waste gas whether the second, or the first and the third part of the waste gas is recirculated.

Table4 Different modes of Waste Gas Recirculation.

No waste gas recirculation	Waste Gas Recirculation (WGR)	Selective Waste Gas Recirculation	
		EPO (2nd section)	SWGR (1st + 3rd section)
All waste gas is going to dedusting equipment and afterwards to stack.	A part of the waste gas from waste gas collecting duct is taken after the waste gas fan and is brought back to the sinter process. For this mode, it is not possible to select the waste gas of individual wind boxes.	The waste gas coming from individual wind boxes can be selected. Thus, a part of the waste gas coming from individual wind boxes is recirculated back to the process, the other is going to the gas cleaning equipment and to the stack.	
		The waste gas from the 2nd section is recirculated back to the sinter process. The waste gas from the 1st and 3rd section is going towards cleaning equipment and the stack.	The waste gas from the 1st and 3rd section is recirculated back to the sinter process. The waste gas from the 2nd section is going towards cleaning equipment and the stack.

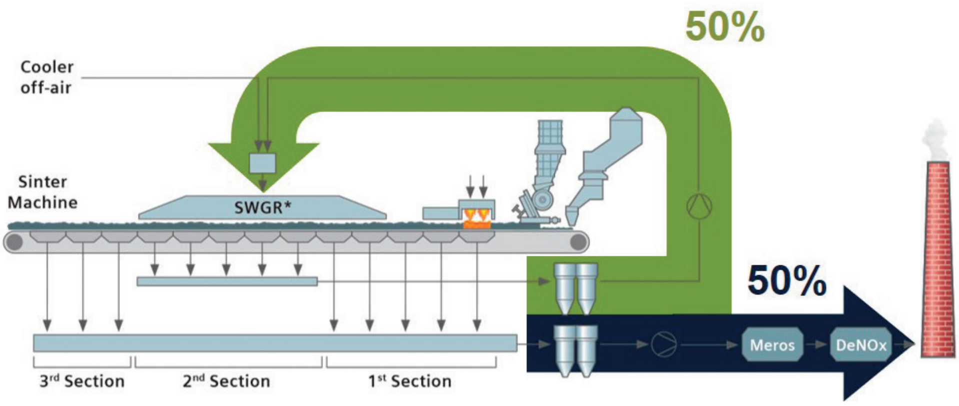

Fig.7　Waste gas recirculation of 2nd section.

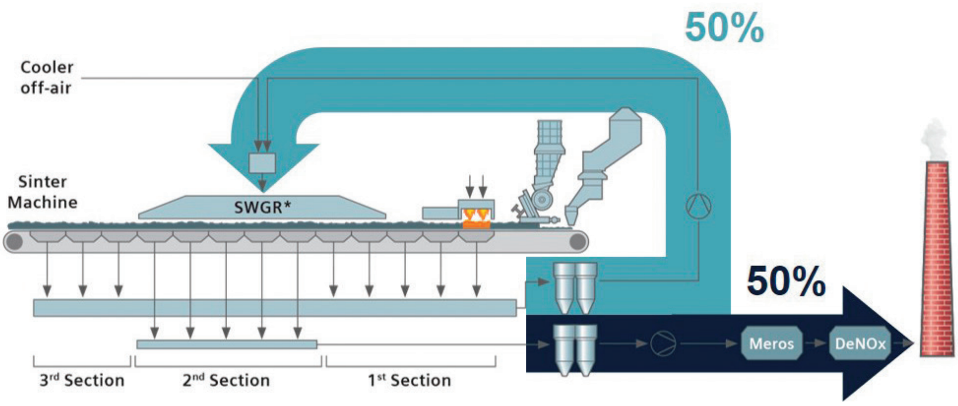

Fig.8　Waste gas recirculation of 1st + 3rd section.

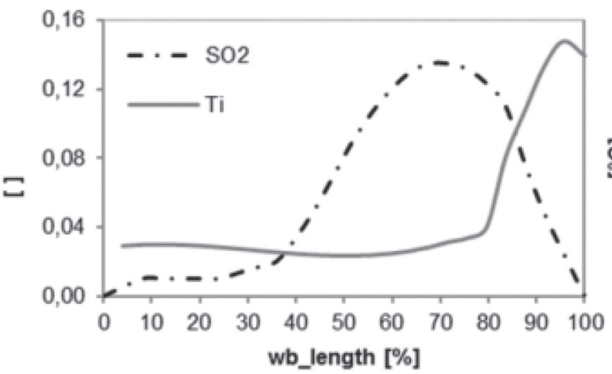

Fig.9　Normalized distribution profile for temperature Ti and SO_2.

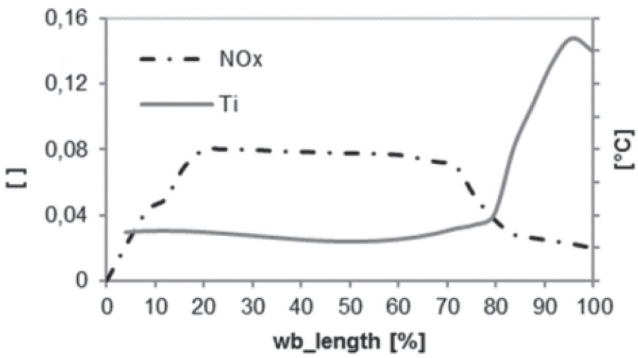

Fig.10　Normalized distribution profile for temperature Ti and NOx

Depending on the composition of the sinter mix and other operational conditions, the selected area along the sinter strand varies. Therefore, in order to ensure an optimized gas recirculation with respect to the burn-through point and the concentration of dust and pollutants in the waste gas stream, the waste gas flow through the individual wind boxes can be independently directed either to the MEROS waste-gas cleaning or back to the sinter strand for recirculation purposes. This is a unique feature for the SWGR which enables an optimum response to varying operational

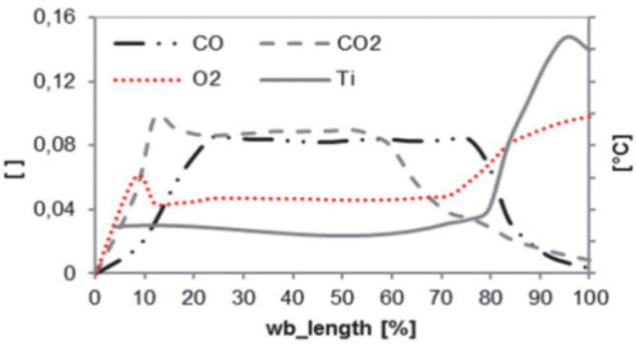

Fig.11　Normalized distribution profile for CO, CO_2 and O_2.

conditions and is thus a decisive factor for the high degree of flexibility of the system.

Different solution will be selected based on customer's specific consideration, as shown in Table5.

The first waste gas recirculation system in Japan is actually be realized at JFE Fukuyama works.

- The sinter waste gas recirculated to the surface of the sinter bed has sufficiently high oxygen content and a temperature which is well above the critical dew point.

Table5 Reference installations of the SWGR System

Reference	Sinter Plant area	SWGR Configuration	Recirculation Rate
voestalpine Linz, Austria: 2005	250 sqm	Recirculation of section II	Approx. 30%
Dragon Steel Corporation, Sinter Plant No. 1, Taiwan: 2009	248 sqm	Recirculation of sections I & III	Approx. 35%
Posco, Pohang, Sinter Plant No. 3, South Korea: 2010	504 sqm	Recirculation of section II	Approx. 20%
Posco, Pohang, Sinter Plant No. 4, South Korea: 2010	517 sqm	Recirculation of section II	Approx. 20%
Dragon Steel Corporation, Sinter Plant No. 2, Taiwan: 2012	387 sqm	Recirculation of sections I & III	Approx. 40%
Jindal Steel & Power Limited (JSPL), India: 2017	490 sqm	Recirculation of section II	Approx. 50%
Metinvest - EMZ, Ukraine;	450 sqm	Recirculation of section II + I & III	Approx. 50%
Shansteel Rizhao, Sinter plants #1 & #2, 2018	550 sqm	Recirculation of sections I & III	Approx. 40%
JFE, Sinter Plant, Japan: 2019	387 sqm	WGR	14 - 50%
JSW Toranagallu SP4	224 sqm	WGR	Approx. 30%
Jianbang Shanxi	378 sqm	WGR	Approx. 35%

- The recirculation hood installed above the sinter machine is equipped with a special sealing system to avoid recirculated waste gas containing carbon monoxide being able to escape into the environment.

The temperature in the waste-gas recirculation hood is typically between 130-200℃. After passing through a gas-mixing chamber, the waste gas mixed with hot air is conveyed to a hood above the sinter strand (see Fig.12). As a special feature of the Waste Gas Recirculation System, the sintering strand is not fully enclosed by the hood structure. It terminates at the side of the pallets where a non-contact, narrow-gap labyrinth seal prevents re-circulated waste gas and dust from exiting to environment. This provides a high degree of safety against CO gas from escaping to the surroundings due to the prevailing low negative pressure. Additionally with this solution, a limited amount of secondary air is drawn into the system.

As mentioned, the recirculation hood does not necessarily extend to the end of the sinter strand, and this allows fresh air to be drawn through the sinter bed in the area of the last wind boxes, which cools the upper sinter layer more efficiently. Likewise improves accessibility of the open pallets offers additional advantages for maintenance work.

Due to the application of the (S)WGR system a downstream MEROS waste gas cleaning plant can be designed significantly smaller in capacity and the required additives for the subsequent DeSOx are reduced.

4 MEROS By-Product Leaching

A specific leaching process has been developed by Primetals Technologies to treat the by-products produced during the MEROS SBC process. Even the MEROS SBC process is highly efficient and the by-product generated

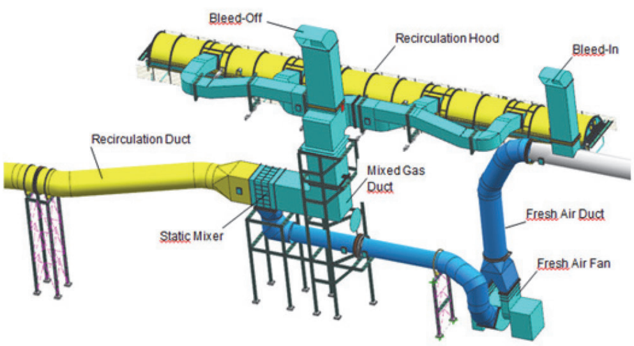

Fig.12 3D Model of a WGR System

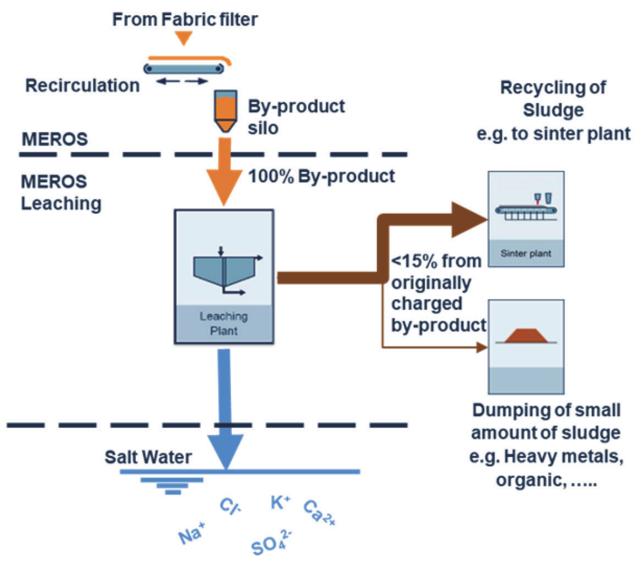

Fig.13　Principle Leaching Process Flow Sheet

is low, a certain amount has to be disposed. For sinter plants situated close to the sea the leaching process is an attractive option to reduce the by-product to about 10%. The by-product contains mainly sodium sulfate and other soluble substances. Hence, a leaching process can be used to dissolve major share of this by-product. The leaching process can be mainly seen as a waste-water treatment plant which ensures clean water discharge conditions which fully comply with all national standards. Fig.13 provides an overflow of the leaching process.

The MEROS by-product is dissolved (leached) in a batch operation. The insoluble part of the by-product (mainly iron oxides, lime, quartz, carbon) is then filtered. This portion can be usually be recycled to the sinter plant, BF or BOF as these are valuable compounds. The leaching water is treated in a sequence of different continuous treatment steps to remove heavy metals, organic compounds and if required also nitrogen and fluorine. Finally the pH is adjusted and the cleaned brine (salt water) passes a final sand and activated carbon police filter before being discharged to the sea. The discharge water is permanently controlled and analysed to ensure compatibility with all standards.

5 Summary & Conclusions

Ever stricter regulations by governmental institutions require lowest emission levels for existing and greenfield iron- and steelmaking plants.

The dry gas cleaning technology (MEROS®) reduces the emissions of SO_2, heavy metals and dioxins from sinter plants safely below the required emission levels. Such low emission levels are maintained by a multi-component additive injection upstream of a high-performance fabric filter, while the installation of a (selective) waste recirculation technology minimizes the investment cost for the gas treatment.

Residues and by-products arising from the gas treatment are often disposed, leading to consumption of valuable landfilling volume and high cost as such material has to be stored under special conditions to avoid uncontrolled leaching of salts and heavy metals.

The innovative leaching process is closely linked to the MEROS plant and minimizes on site the residue volume. After dissolving of the residue a series of treatments steps of the waste water ensure the compliance with the most stringent discharge emission limits prior to the release of the clean brine into the sea. The proposed solutions can be applied to existing and greenfield plants.

The references over the last decade show a high capability of installing the MEROS technology and the waste gas recirculation in greenfield and retrofit sinter plants and meet strictest emission limits.

References

1）BAT Best Available Techniques Reference Document for Iron and Steel Production; Industrial Emissions Directive 2010/75/EU; Integrated Pollution Prevention and Control, https://eippcb.jrc.ec.europa.eu/reference/BREF/IS_Adopted_03_2012.pdf

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