Master Thesis

MEROS Dust Quality of Different Plants and Its Potential Further Uses

submitted by

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in the framework of the Master programme

Food Science and Technology

in partial fulfilment of the requirements for the academic degree

Diplom-Ingenieur

Vienna, May 2022

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Wien, 10.04.2022   Claudia HLEDIK

Acknowledgement

First of all, I want to thank my supervisor Prof. DI Dr. Maria Fürhacker, who made it possible for me to write this thesis and who stood by my side at all times throughout my engagement at the university to support me with her knowledge and experience. I would also like to thank DI Dr. Martin Goetz from Primetals Technologies, who brought this project to the university and made it possible.

I would like to acknowledge my co-workers of the chemical laboratory of the SIG, who welcomed me warmly from the beginning and always supported and advised me with my research and questions. Particularly, I would like to express my gratitude to the student assistant Julian Fränkel for his constant support and friendship. My greatest thanks go to my family, who supported me in every living situation and helped me becoming the person who I am today. I would also like to thank my friends, who always provided me with advice and encouragement throughout my years of study.

Finally, I would like to acknowledge the University of Natural Resources and Life Sciences, Vienna, which made it possible for me to have a great period of study.

Foreword

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Abstract

Sintering is a thermal agglomeration process as preliminary stage for the blast furnaces. During the sintering process high amounts of toxic dusts and gaseous emissions are produced and have to be removed by gas cleaning processes like the MEROS systems (Maximized Emission Reduction of Sintering). The objective of this thesis was to characterize and compare the dusts from the MEROS systems of two sintering plants and different charges.

For the characterization of the the untreated dusts some heavy metals were analyzed. The water soluble propotions of the dusts were determined and in the waterphase the dissolved heavy metals, some ions, the dissolved organic carbon (DOC) as well as the total nitrogen (T-N) were analyzed. The measured parameters in the waterphase were compared to the emission standards from various countries and should provide the basis for the development of necessary treatment methods of the waste water. As additional research topics the evaluation of depositing the dusts in landfills and the reuse of the dusts in the primary sintering process were selected.

The results showed significant differences among the analyzed parameters of the MEROS dusts between the two sintering plants as well as within the charges. The dusts contain high amounts of salts, indicating that 84–94 % of the total mass are soluble in water and the majority of the determined parameters in the produced waste water exceeded the emission standards from various countries. As a result, treatments of the waste water are necessary to fulfill the restricted values and the methods have to be adjusted to the dust compositions. Due to the high salt amounts a direct reuse in the sintering plants is not possible. Depositing is the current main solution for managing such dusts, with the side effect that some bioaccumulative heavy metals and the soluble salts can possibly cause environmental risk.

Kurzfassung

Sintern ist ein thermisches Agglomerationsverfahren als Vorstufe für die Hochöfen. Während des Sinterprozesses entstehen große Mengen an giftigen Stäuben und Gasemissionen, die durch Reinigungsverfahren wie in MEROS-Anlagen (Maximized Emission Reduction Of Sintering) entfernt werden müssen. Ziel dieser Arbeit waren die Charakterisierung und der Vergleich von Stäuben aus MEROS-Systemen zweier Sinteranlagen und unterschiedlicher Chargen.

Zur Charakterisierung der unbehandelten Stäube wurden einige Schwermetalle analysiert. Die wasserlöslichen Anteile der Stäube wurden bestimmt und in der Wasserphase die gelösten Schwermetalle, einige Ionen, der gelöste organische Kohlenstoff (DOC) sowie der Gesamtstickstoff (T-N) analysiert. Die gemessenen gelösten Parameter wurden mit den Emissionsstandards verschiedener Länder verglichen und sollen die Grundlage für die Entwicklung notwendiger Behandlungsmethoden des Abwassers liefern. Als weitere Forschungsthemen wurden die Bewertung der möglichen Deponierung der Stäube und die Wiederverwendung im Primärsinterprozess ausgewählt.

Die Ergebnisse zeigten signifikante Unterschiede zwischen den analysierten Parametern der MEROS-Stäube der beiden Sinteranlagen sowie innerhalb der Chargen. Die Stäube enthalten hohe Salzmengen, wodurch 84–94 % der Gesamtmasse wasserlöslich sind und die Mehrheit der ermittelten Parameter im produzierten Abwasser die Emissionsnormen verschiedener Länder übersteigen. Daher ist eine Behandlung der Abwässer zur Erfüllung der Grenzwerte erforderlich und die Verfahren müssen an die Staubzusammensetzung angepasst werden. Aufgrund der hohen Salzmengen ist eine direkte Wiederverwendung in der Sinteranlagen nicht möglich. Deponierung ist derzeit die Hauptlösung zum Umgang mit solchen Stäuben, mit dem Nebeneffekt, dass einige bioakkumulierbare Schwermetalle und die löslichen Salze möglicherweise eine Umweltgefährdung verursachen können.

1. Introduction

The iron and steel industry has developed to an important player in the everchanging global market over the last years. The raw material scenario is changing continuously with respect to quality and quantity (availability) and the pressure to address global climate change issues increases rapidly, especially because the steel industry is highly energy and carbon intensive. In developing countries like China and India the importance of steel production is growing continuously, so the steel industry in these countries will play an important role in defining and shaping the future of the industry. Important competitions taken by the steel industry to address climate change risks are the minimization of greenhouse gas emission and energy consumption as well as the optimization of recycling the steel scrap [1]. During a sinter process several chemical and metallurgical reactions takes place and beside the sinter also high amounts of toxic dust and gaseous emissions are produced [2]. Primetals Technologies has developed a gas cleaning system called MEROS to treat and remove toxic dusts and components from the flue gas of sintering plants [3].

1.1. Iron ore sintering process

Sintering describes a thermal agglomeration process to manufacture a product with its suitable thermal, mechanical, physical and chemical characteristics being fed to a blast furnace. A mixture consisting out of iron ore fines, agents, and solid fuels (coke) is loaded onto the sinter strand. There the mixture of raw materials is partially melted at a temperature between 1300-1480°C. Next, it undergoes a series of reactions and is getting granulated to form the sinter cake which is then loaded into the blast furnace to produce pig iron [4].

Sintering causes air pollution because the sintering flue gases contain dust, CO_x, SO_x, NO_x, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), polychlorinated (PCDD) and polybrominated dibenzodioxins(PBDD) and furans (PCDF), acid gases (HF, HCl, etc.), heavy metals, alkali metals, organic C and other pollutants. The fuel gas from the sintering plants accounts for approximately 40 % of the total volume of waste gas in the iron and steel industry. The main sources of CO_x, SO_x, NO_x etc. are the solid fossil fuels used such as coke and anthracite. Beside the fuels, also operating conditions contribute to a high air pollution [5].

The emissions of PCDD/Fs from various sources have become a serious environmental issue and the iron ore sintering process has become a major emission source of PCDD/Fs in many countries due to more and more rigorous standards that have been enabled for the control. For example the UN Environmental Program has recommended the emission level of PCDD/Fs <0.2TEQ Nm^3 (dioxins and furans) for new installed iron sintering plants with best available technologies [6]. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives can be formed during the incomplete combustion of fossil fuels and are known as harmful to human health. The iron ore sintering process has been classified as one of the significant PAH emission sources due to the massive burning of coal and coke but no PAH emission standard to mitigate this issue has been defined yet. The high amounts of total volatile organic C in sinter off gas are affected by the coal and coke ratio in sinter raw materials [5, 7]. The amount of heavy metals, alkali metals, SO_x and NO_x depends on the composition of the sinter feed and the chemical and physical properties of each.

The dust is a two components mixture out of coarse dust with a gran size of about 100 µm and the fine dust with a gran size of 0.1 – 1 µm. The coarse dust is originated in the sinter feed as its composition relates to that. The fine dust is formed in the sintering zone after the water evaporation of the mixture. This component is formed during the sintering process itself and consists of alkali and lead chlorides [6]. The pollutants need to be removed from the flue gas with gas cleaning systems.

1.2. MEROS process

MEROS is a dry-type gas cleaning process (Maximized Emission Reduction Of Sintering) developed for the removal of dust and harmful metallic and organic components from the sinter flue gas [3]. The publication of Primetals Technologies in 2020 describes two differnet types of process operations. The first process step in type A is the injection of lignite coke and hydrated lime in the gas stream as absorbent for desulfurization of the off gas (DeSO$_x$) and the reduction of heavy metals, PCDD/F and other toxic organic compounds. As a next step, the gas is moisturized and cooled to a temperature of about 90-100 °C through the injection of water and air in a conditioning reactor. Finally, the dust and trapped pollutants are removed from the off gas by using a pulse jet filter equipped with special high-performance fabrics. In type B sodium bicarbonate can be used as desulphurization agent instead. This variant is used if high DeSO$_x$ degrees are required and a DeNO$_x$ plant is necessary or where land-filling costs are high.

1.3. Current situation of dust management

The byproducts from gas cleaning systems are labelled as hazardous waste because of the contained toxic components and the current main end solution is the disposal in secure landfills. Heavy metals (especially Pb and Hg), soluble salts and other inorganic components are bioaccumulative and due to that the waste has to be immobilized during a pretreatment step to prevent the release of the toxic components in the environment. Immobilization can be reached by adding cement or chelating agents which results in the toxic components becoming chemically inert as well as reducing the migration and diffusion [8].

An alternative possibility is the reuse of the dust as secondary construction material in the sintering plants. Gererally the recycled materials are rich in Fe and C but there are constraints on the recycled materials because operational problems have to be avoided in sinter plants and in blast furnaces and the recycled residues also have some effect on sinter quality, strength and productivity. Especially the concentration of Zn and alkali metals (Na and K) has to be controlled to avoid problems in blast furnaces [9].

Zn is naturally contained in the sinter material (approx. 70–200 g/t sinter feed) but the total amount of Zn in the charge for the blast furnace is usually restricted to 100 g/t–150 g/t of hot metal produced because only a small fraction of the Zn feed is volatilized in the sinter plant. Zn can form crusts in the upper part of the blast furnace and accumulates in the lining which consequently deteriorates [6, 9].

Alkalis, also in small amounts, can rapidly accumulate under high temperatures and influence the productivity of the blast furnace. The alkalis attack the refractory lining in the furnace and are responsible for the scaffolds and lower the life of the reactor [10]. In addition alkalis forming toxic compounds under extreme temperatures as otherwise these can get released into the cleaned

exhaust gas and into the aerial environment [11]. Before the reuse, soluble components such as K and Na have to be lowered to an acceptable level. It is obtained that the mass contribution of KCl and NaCl is up to 40 % in the dust. As a result leaching the dust in water is a possibility to remove the high amount of soluble salts and lower the total dust amount [12].

2. Objectives and research questions of the study

2.1. Objectives of the study

The objective of this study was the characterization and comparison of dusts from MEROS plants and different charges of two different sintering plants taken over a time period of 2 years. The parameters that were determined for the characterization are the solid residues, DOC, T-N, a number of total and dissolved heavy metals as well as some anions and cations. The next step was the evaluation of reutilization of the dusts in the sintering plants. The results of the analysis should serve a basis for the development of removal methods of specific parameters by taking into consideration regulations and emission standards in the respective countries of investigation.

2.2. Research questions of the study

- What are the differences in the compositions of the dusts from two plants A and B?
- Are there any significant differences within the charges from these plants?
- Which components are dissolved in the water phase? What is the characterization of the eluates?
- Fulfill the parameters in the waste water (eluates) produced the emission standards?
- Are any treatments necessary?
- Is it possible to deposite the dusts?
- Is it possible to reuse the untreated dust or the insoluble fraction after the leaching process in the sintering plants?

3. Materials and methods

3.1. Sintering plants and sampling

The dusts were taken from the byproduct silos of two different sinter–MEROS networks. Samples A-D1 to A-D6 were taken from an Austrian plant. This plant has a size of 250 m^2, a sinter capacity of 7920 t/d and a waste gas stream of approximately 600,000 Nm^3/h. The smaples B-D1 and B-D2 were taken from the second plant (plant B), which is located in Asia. This plant has a size of 400 m^2, a capacity of 14,200 t/d the waste gas stream is approx. 1,000,000 Nm^3/h. The byproduct formation of Plant A and Plant B were between 60 and 70 % and approx. 620 kg/h and between 95 and 97 % with approx. 4570 kg/h [13]. Solid samples of A-D1 to A-D5 and B-D1 and B-D2 were taken in small sample sizes of about 2 kg and from sample A-D6 about 120 kg were taken directly out of the MEROS byproduct silos. The samples were taken from different charches over a time period of two years.

3.2. Preparation of liquid samples

As liquid samples, suspensions of 100 g dust and 1 L of deionized water (1:10 w/w) in a volumetric flask were prepared. The mixture was eluated for 120 min by shaking in an overhead shaker. Afterwards, the suspension was centrifuged for 10 min at 4000 rpm to separate the undissolved constituents, and the fine fraction was removed by membrane pressure filtration (cellulose nitrate, 47 mm diameter, pore size of 0.45 µm). The filtered 1:10 solution is the liquid sample and is called eluate (i.e., A-Dn-E).

3.3. Analytical methods

The dissolved fraction (eluate A-Dn-E) was analyzed for dissolved organic C (DOC), total N (T-N), some ions and heavy metals. The DOC and the T-N were analyzed in a Shimadzu (Shimadzu TOC V CPN). Cations and anions in the eluates were separated by a liquid chromatograph (DIONEX ICS 3000, DIONEX Softron Germering, Germany) equipped with an autosampler, suppressor and detected by conductivity.

Heavy metals were measured in the eluates as well as the in solid samples. For determining the total concentration of heavy metals in the dust, the solid samples were digested in a microwave with HNO$_3$ suprapur (65 %). The heavy metal components were determined by means of ionized plasma and detection by mass spectroscopy (ICP-MS, ELAN DRC-e, Perkin Elmer, Waltham, MA, USA).

For the determination of the suspended solids (SS), 200 mL of a 1:10 suspension of dust and water was filtered (cellulose nitrate, 47 mm diameter, pore size of 0.45 µm) in small portions using about 15 fresh filters. Each individual filter was dried before and after filtration at 100 °C for 2 h, cooled in a desiccator and weighted. The percentage of the solid residue was calculated basing on the initial weight of the dust.

4. Results and Discussion

4.1. Characterization of the dusts and eluates

The characterization showed significant differences among the analyzed parameters of the MEROS dusts between the two plants A and B as well as between the charges. First the DOC, T-N and solid residues of the eluates from the dusts A-D1 to A-D6 and B-D1 as well as B-D2 were analyzed (Figure 1). DOC values of plant A samples were in a range between 0.3 and 0.8 mg/g dust. In comparison, the dusts from plant B showed lower contents of soluble organic C, in particular 0.2 and 0.4 mg/g dust. The quantities of total nitrogen were similar across all dusts samples used, between 1.6 and 2 mg/g dust. The solid residues from plant A were generally higher (8 to 12.6 %) than from plant B (6 to 8 %). The parameters DOC, T-N and solid residues did not show significant differences between the two plants A and B and their charges.
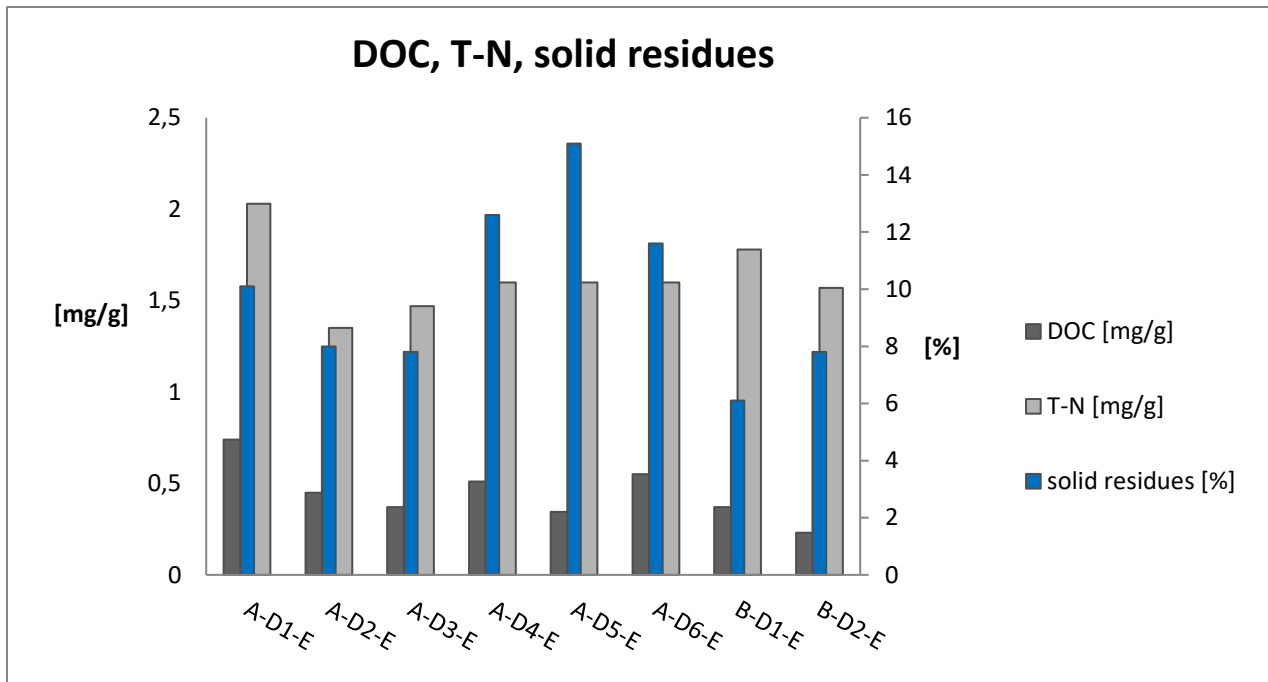
Figure 1. DOC, T-N and the solid residues of eight dusts and eluates.

A significant proportion of the dusts contain soluble salts that can reach the aqueous phase by leaching and form the eluates. 87 to 94% of the untreated dusts were soluble in water. After leaching the dusts in water in a ratio of 1:10 (w/w) the ions Cl, F, SO_4, NO_3, Na, Mg, NH_4, Ca and K were analyzed. The results showed that SO_4 and Cl concentrations form the highest anion concentrations in all dusts representing. They concerned 44 % (m/m) and 13 % (m/m) of the total dry matter of the dusts. The SO_4 concentrations were higher in the eluates from plant B whereas the Cl concentrations were higher in the eluates from plant A. Na and K formed the highest amounts of cations in the eluates from plant A. In the aqueous phase of plant Bs' dusts, merely high concentrations of Na (approximately 30,000 mg/L) were measured. All other ions were present in minor concentrations. Hence, results showed differences between the two plants and

also within the charges of plant A but no significant variations between the two charges of plant B [13].

In the dusts and eluates of the samples A-D1, A-D2, A-D6, B-D1 and B-D2, some total and dissolved heavy metals were detected. All analyzed dusts from plant A showed ways higher Pb_{tot} and Fe_{tot} concentrations than the dusts from plant B. The concentrations of Cr_{tot} and Ni_{tot} appeared in similar concentration ranges in both plants. The amounts of remaining heavy metals like Cd_{tot}, Cu_{tot}, Mn_{tot} and Hg_{tot} were higher in all dust samples from plant A. The highest Zn_{tot} concentration was measured in the dust B-D1 and the concentrations in the dusts from plant A were lower. There were variations within the charge of plant A which could be due to the compositions of the sinter feed used. Within the charges from plant B no significant differences could be found [13].

In the eluates A-D1-E, A-D3-E, A-D6-E, B-D1-E and B-D2-E the concentrations of dissolved heavy metals were analyzed. Beside the DOC, T-N and some ions also the heavy metals have to be removed in case they exceed the emission standards. In general, the results showed lower heavy metals concentrations in the eluates from plant B compared to plant A. In addition, high variations of the concentrations were also measured within the charges from plant A. The majority of the heavy metals remained insoluble in the solid phase, except in the dusts from plant A, where approximately 20 % of Cd, Se and Zn were soluble. In the dust samples from plant B more than 50 % of Cu and Se got dissolved in the aqueous phase [13].

4.2. Comparison with emission standards

The produced eluates can be seen as industrial waste water and quantities have to comply with emission standards of Korea, Japan, China and Austria. In case the concentration of a parameter exceeds a predefined critical value, the components have to be removed. All measured concentrations are compared without distinguishing between the plants and the charges and all parameters except the pH value, T-P and Ni_{dis} exceeded the critical values. For some parameters the lowest measured concentrations did not exceed the threshold value. All previous results showed high variations in all parameters between the two plants. Beside the different present concentrations, the emission standards differ depending on the respective country. These findings build the basis to find potential treatment methods and their performance requirements.

As a result treatments of the eluates are necessary to fulfill the defined emission standards. Depending on the deviations between the samples of one plant and also between the two different plants, the reducing or removal methods have to be adjusted according to the compartments of the raw materials of the sintering plants**.**

Disposal of the byproducts leads to huge amounts of hazardous waste that can lead to bioaccumulation of some heavy metals like Pb and Hg. The high water solubility of Pb, Zn and Se can lead to leaching of the heavy metals and the salts into the environment without any form of stabilization. Leaching as a treatment step is a possible method to reduce the amount of waste and to remove the watersoluble elements especially the salts for depositing the residue. The undissolved residue has a cement-like composition and can be used as a cement additive. The problematic Cl compounds for the sintering process are removed by leaching [11].

One question was whether it makes sense to reuse the untreated dust and the residue after the leaching process in the primary sintering process as feed additive. Zn appears naturally in the

sinter feed and the amount of Zn in the direct dust reused as well as the reuse of the residue will be about 0.6 – 1.7 % of the naturally occurring content. The amounts of Zn do not exceed the prescribed value in the sinter feed. Problematic is the fraction of Na and K. In the direct recycling, the K amount adds about 583 g per t sinter feed. This leads to an increase of the total amount for more than 100 % compared to prescribed K value of 600 – 1000 t/g sinter feed. The Na content in the untreated dust of 1175 g/t sinter feed in direct reuse, increases the Na content about 300 % compared to the prescribed amount of 250 – 500 g/t [6]. In case of reuse of the insoluble residue after washing out the salts with water the amount of K is about 19.6 g/t and 14.4 g/t sinter feed for Na. A leaching step will be necessary to remove the high amounts of K and Na for the recirculation in the primary process.

5. Conclusion

The byproducts of the MEROS plants from two different sintering plants A and B and their eluates differ significantly in their Na, K, Cl, SO_4, Fe and Zn concentrations. Variations could also be measured in other analyzed parameter but only to a less extent. Differences were also analyzed in the dust samples between the charges. For plant A, the highest variations were measured in DOC, Pb_{dis}, Cd_{dis}, Cu_{dis}, Mn_{dis}, and Zn_{dis}. The samples of plant B did not show noteworthy differences within the two charges. Leaching of the dust samples with water led to transfer of all salts into the aqueous phase. The majority of the heavy metals remained in the undissolved solid phase except in the dusts from plant A over 20 % of Cd, Se and Zn were solved. In the samples from plant B over 50 % of Cu and Se got into the aqueous phase.

The produced waste waters (eluates) do not fulfill the emission standards but the parameters that exceed the limitation values differ depending on the plants and their charges. Depending on the initial concentrations of the critical parameters, different treatments steps are necessary to fulfill the standards. The treatments need to be adjusted according to the compositions of the eluates. To find the right removal methods the knowledge of the initial concentrations of the limited parameters is necessary. Generally a reduction or removal of DOC, T-N, F and some heavy metals is unavoidable.

The recirculation of the untreated dust in the sintering process as feed additive is not recommended because of the high salt amounts, especially of Na and K. For recycling as an additive in the sinter feed, the salts have to be washed out during a pretreatment step. With the removal of the salts, also precursors for the formation of halogens as PCDD/F and PBDD/F such as Cl and Br are removed. The amounts of Zn after leaching do not exceed any restriction value but it is lower than the narually occuring amount in the sinter material.

Beside the removal of the alkalis, leaching as a pretreatment reduces the dust amount of approximately 84 to 94 % for depositing but some bioaccumulative hazardous organic compounds and heavy metals like Pb and Hg still remain in the residue.

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7. Appendix

Publication: „MEROS Dust Quality of Different Plants and Its Potential Further Uses"

MEROS Dust Quality of Different Plants and Its Potential Further Uses

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Abstract: Sintering is a process of agglomeration of fine particles into porous sinters for blast furnaces. During the sintering process, high volumes of sinter plant gas containing high loads of dust, SO_2 and NO_X and toxic pollutants, such as heavy metals (e.g., Hg, Pb, Cr and Cd) and PCDD/F, are emitted. The objective of this study was to characterize dusts of different plants as the basis for suggestions of reutilization and treatment options. Dusts, eluates and residues were produced and DOC, T-N, ions and heavy metals were analyzed. The results show that dusts from different plants are very similar in terms of DOC, T-N, Mg, Ca and many heavy metals and only differ in criteria such as suspended solids and ions such as K, Na, Cl and SO_4. Based on the high levels of alkalis and low levels of iron, direct recycling into the sinter or furnace process is not recommended. The dissolution of the soluble substances in water reduces the MEROS dust by 90% of the weight and extracts the alkalis. The remaining wastewater needs to be treated to reduce DOC, T-N and some heavy metals. The solid residues can be recycled into the sinter to reduce potential PCDD/F, which are attached to the activated carbon.

Keywords: sinter plant; MEROS dust; reutilization

1. Introduction

Sintering is a crucial process in steel mills to prepare the feed for blast furnaces to make iron, whereby iron ore fines, flux, recycled products and coke breeze or anthracite are agglomerated to a porous sinter. Sintering is a very complex process, and about 500 parameters [1] need to be controlled and optimized to maintain a high sinter quality. The productivity of the sintering process depends not only on the raw materials and the returned fines balance but also on having optimum and stable operation conditions, such as charge density control, pallet speed control and adverse ingrediencies [1]. In particular, high alkali levels should be avoided to minimize scaffold formation and additional coke consumption [2]. The recycled waste products generated throughout the ironmaking process require, therefore, special physical, chemical and mechanical properties. Sinter plants are in constant evolution to improve techniques and systems to control the process [1]. During the sintering process, high volumes of sinter plant gas are emitted. These gases contain high loads of dust, SO_2 and NO_X and also a high number of toxic pollutants such as heavy metals (e.g., mercury Hg, lead Pb, chrome Cr and cadmium Cd), polycyclic aromatic hydrocarbons (PAH) and polychlorinated (PCDD) and polybrominated dibenzodioxins (PBDD) and furans (PCDF) [3,4]. Lab experiments also showed high concentrations of up to 34.5 ppm total volatile organic carbon (TVOC), mainly benzene, toluene, xylene and ethylbenzene, in sinter flue gas, which were affected by the coal and coke ratio in sinter raw material [5]. These pollutants need to be removed from the off-gas as the sintering process accounts for an important percentage of the iron and steelmaking emissions [6]. These flue gas purification processes can be classified into two major groups: wet processes and dry processes [7]. To remove SO_2, different systems can be used, such as the circulating

fluidized bed (CFB)–FGD process, ammonia-ammonia sulfate process, limestone/gypsum process, maximized emission reduction of sintering (MEROS)–FGD process and activated carbon adsorption process. Cores et al. [1] described different techniques: the WETFINE technology (developed by VAI) consists of a flexible modular system to reduce dust, alkaline chloride, SO_X and dioxin contents. Gas scrubbing is achieved by a mixed system: wet wash and electrostatic discharges, but this treatment system cannot reduce dioxin emission levels below 0.4 ng I-TEQ Nm^{-3}. For an improvement, urea was added and some plant operating parameters were modified.

In the MEROS process (maximized emission reduction of sintering), developed by Siemens-VAI [8], dust, acid gases, hazardous metals and organic compounds are eliminated with high efficiency rates, and this treatment fulfills current environmental regulations. There are two options of desulfurization agents: option A uses hydrated lime and option B uses sodium bicarbonate. The difference between these two options is the precondition for optimized desulfurization. Desulfurization with hydrated lime requires lower gas temperatures (approx. 100 °C) and a defined moisture level for optimal performance.

Option B injects the additive into the waste gas after the ESP of the sinter plant; to reach a higher efficiency rate, there is an internal recirculation after the pulse jet filter (bag filter). Option B can handle a higher waste gas temperature and does not need a specific moisture content. Additionally, the use of sodium bicarbonate is preferred if a high $DeSO_x$ degree and a $DeNO_x$ plant are requested [9].

The efficacy of the process results in a dust reduction of more than 99% to less than 5 mg/Nm^3; a Hg and Pb reduction of 97% and 99%, respectively; and PCDD/F are eliminated by about 97% and VOCs by more than 99% [10]. This means that MEROS® is currently the most modern and powerful system for cleaning off-gas in sinter plants. Different treatment methods have to be applied to comply with the respective national legislation on the emission limits for each substance, as the plants have to adapt and/or incorporate gas treatment systems to reach their specific emission limits. Although the MEROS process is valuable as it removes acidic components such as HCl and SO_2 up to a very high level, large amounts of residues containing high concentrations of soluble alkali salts, heavy metals and organic pollutants are formed. The gas cleaning residue is considered as hazardous waste, and Song et al. [11] found that Pb and Se are the main elements of environmental and health concern. Therefore, the disposal of residues in landfills must meet special requirements, and solidification/stabilization using cement and a chelating agent were investigated by Song et al. [11]. Solidification/stabilization is a necessary step for the immobilization of heavy metals. The solidification of dust from a $DeSO_x$ plant with cement has the disadvantage of high CO_2 emissions—e.g., 200–550 kg/t fly ash was emitted depending on the ratio of cement and dust [12]. Another argument against the mixture of dust and cement is the high concentration of cement used and the decreased potential of further reutilization [12].

Another option would be reutilization in a primary process step, such as in the sinter plant. However, different ingredients such as Zn and especially high alkaline values show adverse effects on the ESP and in the blast furnace process [2,13]. Another method suggested by Xu et al. [14] is the reuse of the washed residue in cement production. For all of these potential reuse options, information on the composition of the dust and its fractions is required.

In this paper, MEROS sinter dusts from two different plants are characterized, and the differences between various charges and plants are pointed out. The knowledge on the ingredients of the dusts is crucial for potential recycling or reuse options. For reusing purposes, eluates and residues were produced and characterized. One of the main topics of this paper is to find the best solution of reutilization of the dust from a dry $DeSO_x$ plant (Sinter–MEROS network). Therefore, different options and criteria for further applications and uses are suggested.

2. Materials and Methods

2.1. Description of the Plants

Residue samples of sinter waste gas streams were collected from two different sinter plants with MEROS (maximized emission reduction of sintering) gas purification units, called Plants A and B. The two MEROS plants are located in different continents. One plant is located in Asia and the other one in Europe. The following description of the sinter and MEROS plants gives an overview of the plant sizes (design parameters are used).

Samples A-D1 to A-D6 were collected from Plant A, with a plant size of 250 m^2, a sinter capacity of 7920 t/d and a waste gas stream of approximately 600,000 Nm^3/h. Samples B-D1 and B-D2 were taken from the second plant of the Sinter–MEROS network (Plant B), with a size of 400 m^2 and a capacity of approx. 14,200 t/d. The waste gas stream is approx. 1,000,000 Nm^3/h. Both sinter plants are designed for a sinter bed height of 700 mm and applied the bicarbonate process. The designated desulfurization rate and byproduct formation of Plant A and Plant B were between 60 and 70% and approx. 620 kg/h and between 95 and 97% with approx. 4570 kg/h, respectively.

2.2. Sampling

Solid samples of A-D1 to A-D5 and B-D1 and B-D2 were taken in small sample sizes of about 2 kg in PE bottles directly out of the MEROS byproduct silo. From sample A-D6, about 120 kg was taken from the silo of Plant A in 4 different barrels. Due to this, more experiments were conducted with this sample compared to the others.

2.3. Preparation of the Samples

For the lab experiments, 1:10 (mass per volume) suspensions were prepared by dissolving 100 g dust in 1 L of deionized water in a volumetric flask. The mixture was transferred into a plastic bottle and eluted for 120 min by shaking in an overhead shaker. Afterwards, the suspension was centrifuged for 10 min at 4000 rpm to coarsely separate the undissolved constituents, and the fine fraction was removed by membrane pressure filtration (cellulose nitrate, 47 mm diameter, pore size of 0.45 μm). The filtered 1:10 solution is called eluate (i.e., A-Dn-E). The solid fraction after dissolution and removal of the dissolved fraction is called solid residue (i.e., A-Dn-R).

2.4. Analytical Methods

The dissolved fraction (eluate A-Dn-E) was analyzed for dissolved carbon and nitrogen, selected ions and heavy metals. The untreated dust (A-Dn) and the solid residues after filtration (A-Dn-R) (pore size 0.45 μm) were analyzed for total heavy metals and ions. With the unfiltered suspension of dust (dilution of 1:10) and water, the percentage of suspended solids was determined.

The parameters pH, temperature and conductivity were measured with WTW (Multi 3630, Xylem Analytics, Weilheim, Germany).

2.4.1. ICP-MS

For determining the total concentration of heavy metals in the dust and solid residue samples, 2.0 g of the dried (100 °C) solid samples was digested in a microwave with HNO_3 suprapur (65%). The heavy metal components were determined by means of ionized plasma and detection by mass spectroscopy (ICP-MS, ELAN DRC-e, Perkin Elmer, Waltham, MA, USA) in the quantification mode according to DIN EN ISO 17294-1 (E 36): 2003. The results for the solids, such as dusts and filter residues, are given as total (e.g., Cd_{tot}), and in the filtered eluate, as dissolved concentration (e.g., Cd_{dis}).

2.4.2. Ion Chromatography

Cations and anions were separated by a liquid chromatograph (DIONEX ICS 3000, DIONEX Softron Germering, Germany) equipped with an autosampler, suppressor and conductivity detector. An AS15 250 × 2 mm + AG15 50 × 2 mm column was used for anion

separation and a CS12A 250 × 2 mm + CG12A 50 × 2 mm column was used for cation separation. As the mobile phase (eluent) for the determination of the cations, methane sulfonic acid solution was used, and for the determination of the anions, potassium hydroxide solution was used. Anion and cation standards were prepared using stock standards (Merck). All solutions and dilutions were prepared with deionized water. The limits of quantification and working ranges for the different ions were as follows: for anions, 0.25–3.0, 0.22–2.5, 1.0–10, 0.65–4.9 and 0.1–3.0 mg/L for Cl, NO_3-N, SO_4, PO_4-P, F and Br; and for cations, 0.25–6.5 mg/L for Na, Ca and Mg and 0.78–14.8 mg/L for NH_4-N, respectively. Several dilutions of the samples were analyzed to cover the different concentration ranges and stay within the working range of the various ions. The dilutions resulted in different limits of quantification.

2.4.3. TOC, DOC and T-N

The total organic carbon (TOC) and dissolved organic carbon (DOC) (after filtration to 0.45 μm) were analyzed as non-purgeable organic carbon in a Shimadzu (Shimadzu TOC V CPN) at pH to <2 (HCl 32% and sparging); the carbon was oxidized by thermocatalytic combustion to carbon dioxide, which was detected by a non-dispersive infrared spectrometer (NDIR) according to DIN EN 1484 (H3): 2019-04. The working range was between 0.3 and 1000 mg/L C with a standard deviation of 5%. The determination of the total content of bound nitrogen (T-N) was based on its oxidation by catalytic combustion in an oxygen atmosphere at >700 °C to form nitrogen oxides. The nitrogen mass concentration was quantified by chemiluminescence detection (after reaction with ozone). The limit of quantification was 0.1 mg/L T-N with a standard deviation of 9%.

2.4.4. Bulk Density and Suspended Solids

For the bulk density of the dusts, 20.0 g dust was weighed in a 100-milliliter measuring cylinder, and the sample bulk density (g/L) was derived from the mass per volume.

To determine the suspended solids (SS), a total volume of 200 mL of a 1:10 suspension of dust and water was filtered (cellulose nitrate, 47 mm diameter, pore size of 0.45 μm) in small portions using 15–20 fresh filters. Each individual filter was dried before and after filtration at 100 °C for 2 h, cooled in a desiccator and weighed; the sum of all portions was used for the calculation of the percentage of the solid residue based on the initial weight of the dust.

2.4.5. XRD

The untreated dust (A-D6), this untreated dust heated to 550 °C, the dried solid residue (A-D6-R) and the dried salts from the eluate (A-D6-E) were studied by means of X-ray diffraction (XRD) using a Panalytical X'Pert Pro MPD diffractometer (Pananalytical, Almelo, Netherlands) with automatic divergent slit, Cu LFF tube 45 kV, 40 mA, with an X´Celerator detector. The measuring time was 25 s per step, with a step size of 0.017°. The semiquantitative mineral composition of the bulk samples was estimated using Rietveld refinement with the Panalytical software X´Pert (Version HighScore Plus, Pananalytical, Almelo, Netherlands). Simultaneous thermal analysis (STA), thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were performed with the dried residue after filtration. The STA analyses were carried out on Netzsch STA 409 PC Luxx (Netsch, Selb, Germany). Between 50 and 51 mg of the sample was weighed in a Pt-cup and then analyzed in a controlled atmosphere with 50 mL/min air and 10 mL/min N_2. The heating rate was 10 °C/min, and the samples were heated up to 1000 °C. The physical parameter measured in DSC was the difference in energy inputs into the sample and reference material when both are subjected to a controlled temperature program. Endothermal and exothermal reactions could be observed [15]. During TG measurement, mass changes of the sample mass were observed.

2.5. Data Analysis and Statistics

For the heavy metals' concentrations, the data were measured in multiple dilutions and the results were selected according to the dilution in the working range. The data acquisition and processing of heavy metals were controlled by ICP-MS software (ELAN 3.0, Perkin Elmer, Waltham, MA, USA), and the results were expressed in μg/L but recalculated and expressed as μg per g.

In order to determine whether the means of the two sets of dust data from the different plants are significantly different from each other, Student's t-tests were performed for the different parameters using the program R. The level of significance was chosen at 5% (*p*-value < 0.05).

3. Results and Discussion

3.1. Characterization of Different Dust Samples

The variations in concentration between different charges of MEROS dusts of Plant A and between Plants A and B are shown in Figure 1. A high fraction of the dust solids were water soluble and could be transferred into the eluate; only about 10 to 12% of the total solids of dust of Plant A and 6% of the dust of Plant B remained solid and could be removed from the solution with membrane filters. The samples A-D1, A-D6 and B-D1 were examined more closely for DOC, T-N, solid residues, bulk density and total and dissolved heavy metals.
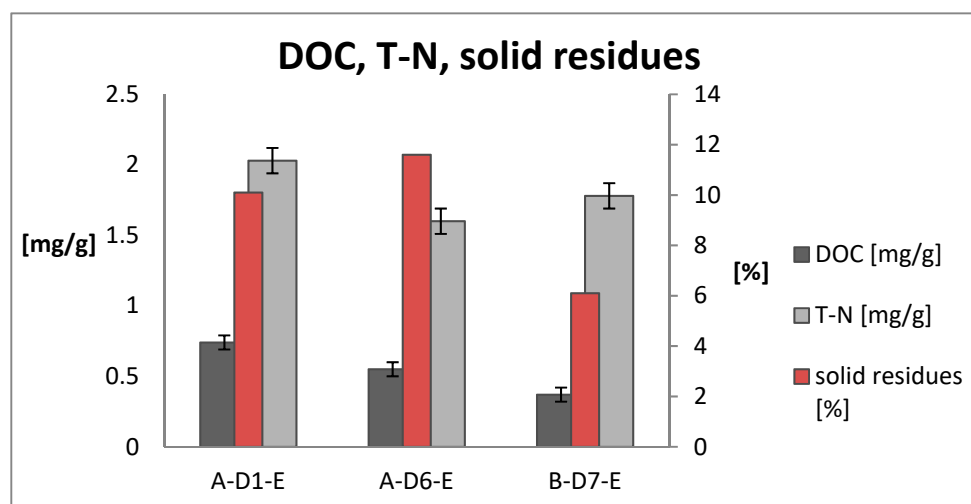

Figure 1. DOC, T-N and the solid residues of the three dusts and eluates.

The bulk density of A-D1, A-D6 and B-D1 was observed to be 400, 278 and 488 g/L, respectively. The data show that the variations within Plant A are higher than those between the two plants. Figure 1 shows the DOC, T-N and the solid residues of the three dusts and eluates.

The DOC concentration in the eluate varies between 0.37 and 0.74 mg/g, and that of T-N between 1.6 and 2.03 mg/g. The statistical analysis indicates that there is no significant difference between the different dusts.

3.2. Characterization of the Different Eluates

A huge fraction of the dust could be dissolved as most of it consisted of ions, as can be seen in Table 1. The dissolved ion concentrations in the eluates A-D1-E to A-D6-E and B-D1-E to B-D2-E after filtration (pore size: 0.45 μm) are summarized in Table 1.

Table 1. Concentration of cations and anions in the eluates of the dusts (dilution 1:10).

Ions	A-D1-E	A-D2-E	A-D3-E	A-D4-E	A-D5-E	A-D6-E	B-D1-E	B-D2-E
Cl (mg/L)	13,000	13,000	13,000	6700	10,000	14,000	3300	2900
F (mg/L)	110	110	90	56	60	90	300	300
SO_4 (mg/L)	50,000	44,000	44,000	44,700	45,000	41,000	66,000	64,000
NO_3-N (mg/L)	150	44	34	n.a.	46	54	7.3	4.4
Na (mg/L)	25,000	24,000	24,000	22,900	21,000	22,100	30,500	29,900
Mg (mg/L)	13	25	18	478	<20	26.1	2.18	2.73
NH_4-N (mg/L)	<5	<5	<5	219	91	122	95	92
Ca (mg/L)	27	60	100	229	n.a.	11.5	37.4	17.2
K (mg/L)	11,000	10,000	10,000	11,000	9500	11,100	521	423

n.a.—not analyzed.

The most important anions are SO_4 and Cl, which make up 44% (m/m) and 13% (m/m) of the total dry matter of the dust, respectively; the major cations are Na and K, contributing 24% (m/m) and 11% (m/m) of the total dry matter, respectively. Due to the high concentrations of ions in the eluate and remaining salts in the solid residue, the calculated value can reach more than 100% of the mass of the dust used; this is potentially due to the overestimation of the solid residue, as the complete removal of the high concentrated salt solution during filtration was not possible, and to reflect practical applications, no washing step was performed. All other ions could be detected only in minor concentrations; PO_4-P was, in most cases, below the LOQ. Although F, NO_3-N, NH_4-N and Br contributed only little to the total mass, some have strict standard values according to wastewater emission regulations. The eluates A-D1 to A-D3 have NH_4-N concentrations <LOD (limit of detection) in contrast to all others. In A-D1-E, quite high concentrations of NO_3-N could be detected. Ammonia can be added into sinter plants to reduce the formation of PCDD/F [3]. The difference between the T-N values and the sum of the fractions of NH_4-N and NO_3-N is organic N, as NO_2-N could not be detected in any sample. The eluates from sinter Plant B had higher concentrations of SO_4 and Na than those from Plant A, which is probably due to the design, as the permit of Plant B requires a higher rate of desulfurization than Plant A does. The K content was lower in the eluates from sinter Plant B.

3.3. Analysis of the Heavy Metals Contained

Selected dusts were also analyzed to gain insight on the heavy metal content of the dusts and the corresponding eluate. The dusts A-D1, A-D2, A-D6, B-D1 and B-D2 were investigated for total and dissolved heavy metals (Table 2). In addition, the data were compared to data in the literature and the effluent standards of different countries.

Although the deviation between the samples of Plant A is high, which could be due to different sinter feeds during the sampling times, the concentrations of heavy metals of Plant B are lower for nearly all metals except Ni and Zn. The total concentration of Fe in the dust was very low in all samples and only between 0.086 and 0.73% of the dust. In comparison to data in the literature, the sample of Plant A "A-D6" was up to one order of magnitude higher in terms of Pb than seen in the data of Sheng et al. [7], who characterized samples from MEROS flue gas desulfurization (FGD) systems, but are in line with the data of Song et al. [11], who found total concentrations of Pb, Cu, Fe Mn, Se and Zn in the dust of a MEROS system in the same order of magnitude (Table 3).

Interestingly, the Fe content of the dust was very low, as also confirmed by XRD investigations, which could mainly detect amorphous material and salts and only traces of iron (Tables 4 and 5). Only parts of the evaporated dried eluate could be quantified. For all other ingredients, their amounts could only be assessed as *** high, ** medium, * low or as traces. Figures 2 and 3 show the X-ray diffractograms of samples A-D6 and B-D2 after different treatments.

Due to the amorphous structure of the sample, a better result could be obtained after the heat treatment at 550 °C. In dust A-D6, mainly NaCl and mixed salts of Na and K with

Cl and SO_4 could be detected; the eluates were very crystalline and could be quantified. In dust B-D2, Na_2SO_4 could be detected. From the XRD results, it is also clear that the residue still contains soluble salts. Sheng et al. [7] characterized samples from two flue gas desulfurization (FGD) systems of two different sinter plants in China. In both dusts, the main mineralogical phases were $CaSO_3$ $1/2H_2O$, $CaSO_4$, $Ca(OH)_2$ and $CaCO_3$.

Table 2. Total concentrations (µg/g dust) of Pb, Cd, Cr, Fe, Cu, Mn, Hg, Ni and Zn in three dusts and the LOQ (after digestion).

Total Heavy Metals	A-D1	A-D1	A-D6	B-D1	B-D2	LOQ
Pb_{tot} (µg/g)	1510	3470	3970	7.7	4.7	0.08
Cd_{tot} (µg/g)	12.1	27	50	0.37	0.25	0.002
Cr_{tot} (µg/g)	3.7	5.1	10.1	9.1	7.4	0.05
Fe_{tot} (µg/g)	3000	4900	7280	877	864	0.2
Cu_{tot} (µg/g)	110	136	78.1	4.7	5.1	0.06
Mn_{tot} (µg/g)	158	249	340	34.5	41.5	0.01
Hg_{tot} (µg/g)	180	319	385	92.5	96	0.012
Ni_{tot} (µg/g)	0.58	0.83	1.4	9.6	7.4	0.04
Zn_{tot} (µg/g)	253	207	259	506	271	0.12

LOQ: Limits of Quantification.

Table 3. Comparison of MEROS dust samples data in the literature.

Heavy Metals	MEROS-FGD [7]	MEROS [11]	A-D6	B-D2
Pb_{tot} (µg/g)	387	2437 ± 76	3970	4.7
Cr_{tot} (µg/g)	4	-	10.1	7.4
Cu_{tot} (µg/g)	-	95 ± 3	78.1	5.1
Fe_{tot} (µg/g)	-	7301 ± 249	7280	864
Mn_{tot} (µg/g)	-	117 ± 6	340	41.5
Se_{tot} (µg/g)	-	76 ± 4	48.5	120
Zn_{tot} (µg/g)	-	154 ± 8	259	270

Table 4. Results of the XRD investigation and semiquantitative assessment.

Material	A-D6	A-D6 (550 °C)	A-D6-R	A-D6-R (550 °C)	A-D6-E
Amorphous Material	***		***		
$(K_{0,2}Na_{0,8})Cl + KCl$ (Sylvin)	**	**			
NaCl	**	**	*	*	11%
$Ca(SO_4)$ (Anhydrite)	traces	traces			
$Ca(OH)_2$	traces				
CaF_2	traces	traces		traces	
$CaCO_3$ (Calcite)			*	*	
$Ca_5[F/OH(PO_4)_3]$				traces	
Fe_2O_3 (Hematite)	traces	traces	*	traces	
Fe_3O_4			traces	traces	
$NaK_3(SO_4)_2$ (Aphthitalite)	*	*			33%
Feldspar			*	*	
SiO_2 (Quartz)			traces	traces	
$MgCa(CO_3)_2$				*	
Mica				traces	
Na_2SO_4 (Thenardite)	traces				55%
Na_2SO_4 (Metathenardite)		*			

Table 5. Results of the XRD investigation and semiquantitative assessment (continued).

Material	B-D2	B-D2 (550 °C)	B-D2-R	B-D2-R (550 °C)	B-D2-E
Amorphous material	***		***		
Na_2SO_4	**	***	*	**	
α-Na_2SO_4 (Thenardite)			*		96%
Na_2SO_4 (Metathenardite)				**	
NaCl	*	*			3%
$Ca(SO_4)$ (Anhydrite)	traces	traces			1%
Fe_2O_3 (Hematite)			traces	traces	
Fe_3O_4			traces	traces	
SiO_2 (Quartz)			*	**	
$Ca_5[F/OH(PO_4)_3]$					traces

3.4. Potential Direct Reuse of the Dust or the Solid Residue after Leaching

Several papers investigated different strategies of disposal such as disposal in a secure landfill (hazardous waste) with adequate solidification [11,12] or reuse of residues as secondary construction materials [14] or as cement additives [7]. However, these papers also discussed the problems of the long-term stability of the cement matrix, independent of whether the dust will be cemented or used as an additive for the cement industry. In conclusion, there is a risk of possible leaching of harmful substances from the sinter dust.

Another strategy could be recycling in the primary process, but the low concentration of iron in the dust makes direct reuse questionable, even more so as the alkaline concentration is very high. Additionally, alkalis (Na, K) are among the elements which have a negative effect on the blast furnace performance (such as Na, K, Pb, Mn, etc.)—those with a very high impact. Zn and evaporated Pb are transported with the upstream of the top gas to the upper area of the blast furnace. The accumulation of Pb on the burden particles reduces the reduction process efficiency of the blast furnace and locks the incineration of the coke, whereas Zn starts to precipitate and builds up scaffolds such as alkalis [16].
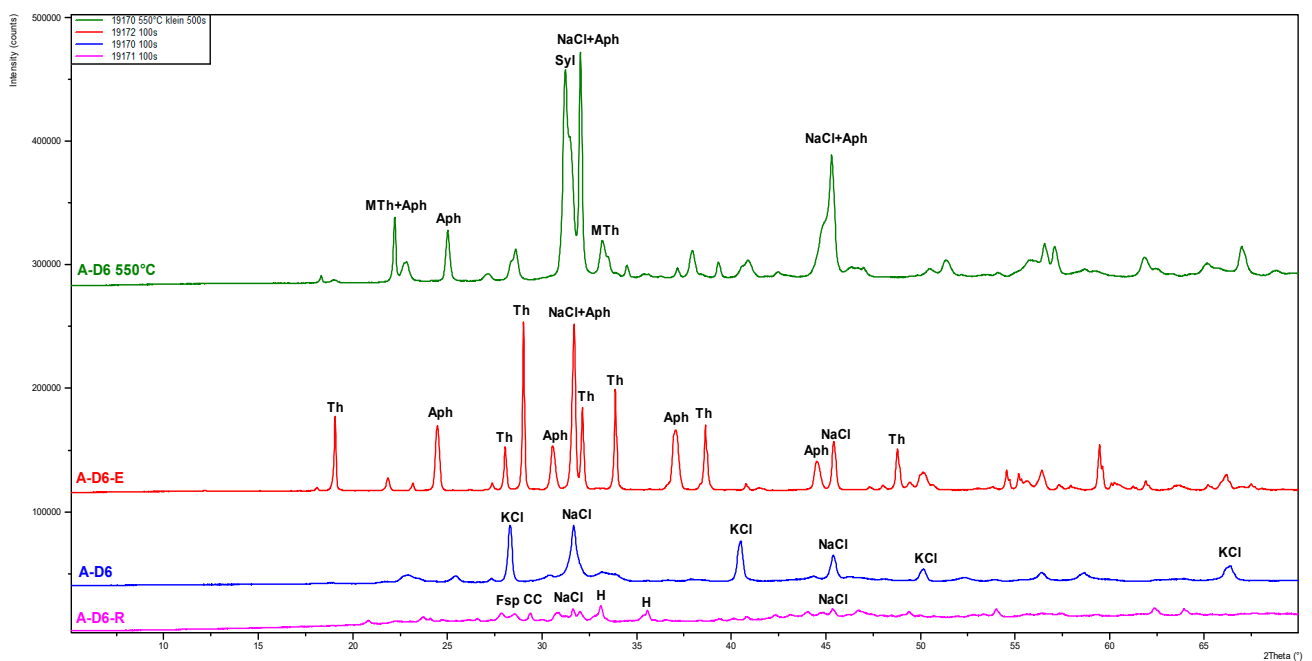

Figure 2. X-ray diffractograms of sample A-D6 after different treatments. Aph = Aphthitalite; Syl = Sylvin; Th = Thenardite; MTh = Metathenardite; Fsp = Feldspar; CC = Calcite; H = Hematite.
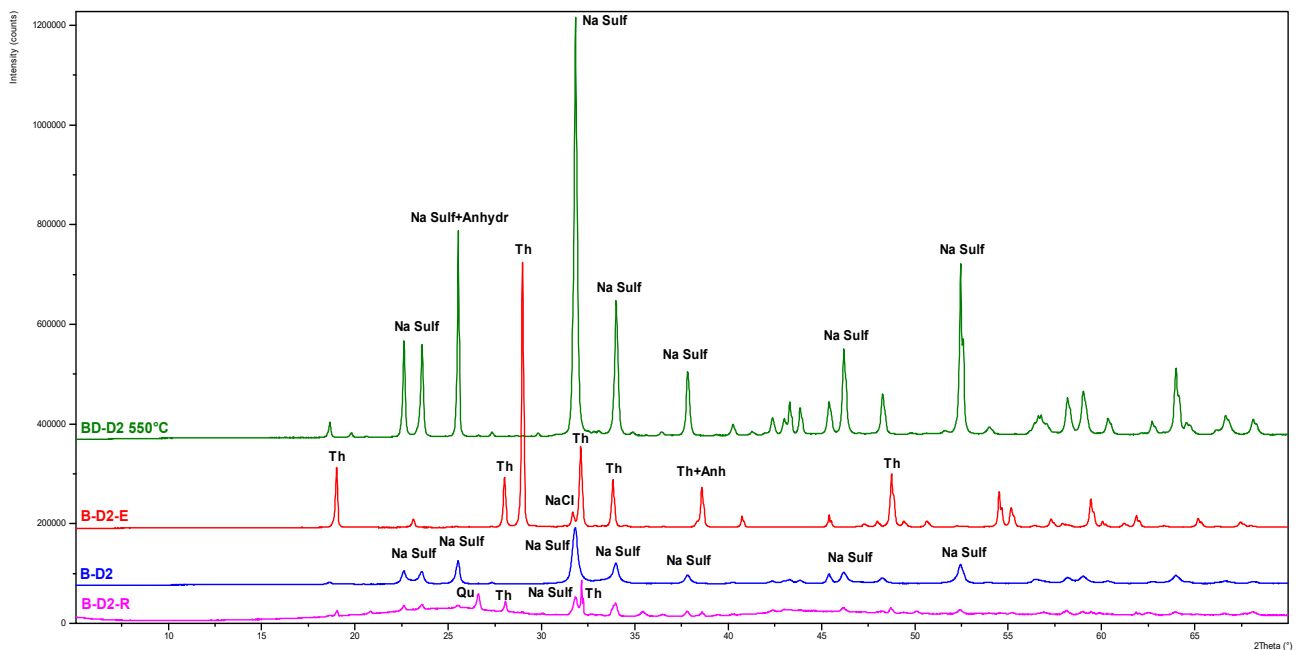
Figure 3. X-ray diffractograms of sample B-D2 after different treatments. Na Sulf = Na_2SO_4; Anhydr = Anhydrite; Th = Thenardite; Qu = Quartz.

For a better overview, in Table 6, the concentrations of Zn and alkalis and their contributions to the sinter material are shown with and without an additional treatment step (washing of the sinter dust), which, in case of reuse, would be charged to the primary process. The values are calculated in g/t sinter feed. The ratio of MEROS dust is approx. 0.5% of the designed sinter capacity.

Table 6. Dust content and contribution to the total sinter of untreated or treated dust.

Salt	Dust Content mg/g	Direct Reuse of the Dust Add-on g/t to Sinter Raw Material	Reuse after Treatment Add-on g/t to Sinter Raw Material
K	123	583	19.6
Na	248	1175	14.4
Zn	0.3	1.2	0.9

Zn will be charged naturally with the sinter material (approx. 70–200 g/t) [13]. Compared to the potential load of Zn, in the case that the dust is recycled to the furnace, the fraction will only be 1.2 g/t—that is, about 0.6–1.7% of the natural content. The results for the alkalis (Na and K) are different. Without a treatment step, the add-on to the natural alkaline amount (for K and Na of 600–1000 and 250–500 g/t sinter feed, respectively [13]) are, for K and Na, 583 and 1175 g/t sinter feed, respectively. The increase in total amount for K is more than 100% compared to the normal value, and for Na, more than 300%.

Geerdes et al. [17] considered an alkaline content of 1 to 3 kg/t HM (hot metal) as the upper limit for the prevention of scaffolds, which is similar to the paper of El Geassy [2], who investigated the correlation between the alkaline content and the presence of scaffolds on the furnace wall, with the result that there is a relation between alkalis and scaffolds. They show the relation of the input of Na_2O to 6–7.5 kg/t pig iron (4.5–5.25 Na kg/t pig iron) and the K_2O feed between 1 and 1.8 kg/t pig iron (0.8–1.5 K kg/t pig iron) [2] and the presence of scaffolds. Based on the above-mentioned limits [17], the contents in Table 6 and under the assumption of a 100% sinter feed with an iron content of 58% to the blast furnace, the alkaline value in the blast furnace will exceed the above-mentioned limit if the MEROS dust will be reused without a treatment step in the sinter plant.

For direct reutilization, a high content of alkali poses a major problem, as the amount of alkali in the burden is split between liquid, solid and gas and depends on the conditions. Liquid and solid streams move downwards, while the gas stream is the opposite. In particular, alkalis in the gas phase are the most critical ones because according to condensation or oxidation processes, the alkalis precipitate [16] and build scaffolds on the furnace walls, which increase the gas velocity and reduce the working volume; the risk of braking off scaffolds is that chilled areas in the blast furnace could occur [2]. In addition, alkalis increase the coke consumption by about approx. 19.6% [2] and also move the equilibrium of the Boudouard reaction to lower temperatures according to catalytical influences [16]. They also have an influence on the physical and chemical properties of the slag, attack the refactoring lining in the furnace [2] and decrease the efficiency of the ESP dust emissions. Dust emissions <50 mg/Nm^3 were only reachable with an alkaline input of below 2.5 kg/t [13].

Therefore, alkalis should be removed from MEROS dust before reuse in sinter or blast furnaces. In our study, the soluble fraction was dissolved with water, which removed about 89–94% of the previous solids of the dust. The remaining wastewater (eluate) contained some DOC, T-N and heavy metals (Table 7) and would need to be treated to remove toxic substances, nutrients and organic carbon.

Table 7. Dissolved concentrations (µg/L eluate) of Pb, Cd, Cr, Fe, Cu, Mn, Hg, Ni and Zn of three dusts and the LOQ (in water).

Dissolved Heavy Metals	A-D1-E	A-D3-E	A-D6-E	B-D1E	B-D2-E	LOQ
Pb_{dis} (µg/L)	3190	519	308	7.7	7.5	0.5
Cd_{dis} (µg/L)	143	1220	1180	4.2	3.2	0.05
Cr_{dis} (µg/L)	40.7	5.5	18	2.2	4.4	0.5
Fe_{dis} (µg/L)	74.3	93.5	172	111	46.6	5.0
Cu_{dis} (µg/L)	1210	148	1070	350	339	1.0
Mn_{dis} (µg/L)	932	3950	2290	312	471	0.5
Hg_{dis} (µg/L)	3400	13,000	2380	19.7	21.9	0.1
Ni_{dis} (µg/L)	1.2	1.8	1.5	5.2	2.6	2.0
Zn_{dis} (µg/L)	154	4890	7070	3440	1290	6.0

Additionally, for the dissolved fractions, huge differences could be obtained between the plants, except for in Fe and Zn. Although some of the concentrations in the wastewater were high, e.g., Pb and Hg, only a small fraction of heavy metals dissolved, depending on the element. Figure 4 shows the total concentration of heavy metals (100%) in dust A-D6 and B-D2 split up in the dissolved fractions (A-D6-E and B-D2-E) and fractions in the solid residues in %. For this comparison, the results for the dissolved fraction were expressed in µg/L but recalculated and expressed as µg per g based on the solids used for the preparation of the eluate.

Most of the heavy metals remained in the solid phase of A-D6; only Cd, Se and Zn showed more than 20% solubility. In the eluate B-D2-E, a special high solubility of Cu and Se could be observed.

The assessment of different options of reutilization indicates that during water treatment, emissions to surface water have to be expected. Therefore, the concentrations in the different eluates were compared to the emission standards of various countries. These standards are either based on national emission levels or selective permits for the metal industry.

Table 8 shows the emission limits of Korea, Japan, China and Austria compared with the values of the investigated eluates A-D1-E, A-D2-E, A-D3-E, A-D4-E, A-D5-E, A-D6-E, B-D1-E and B-D2-E.

The pH value and the amount of T-P and Ni were below the limit values. All other parameters were prone to exceed the acceptable range and require the development of potential treatment options.
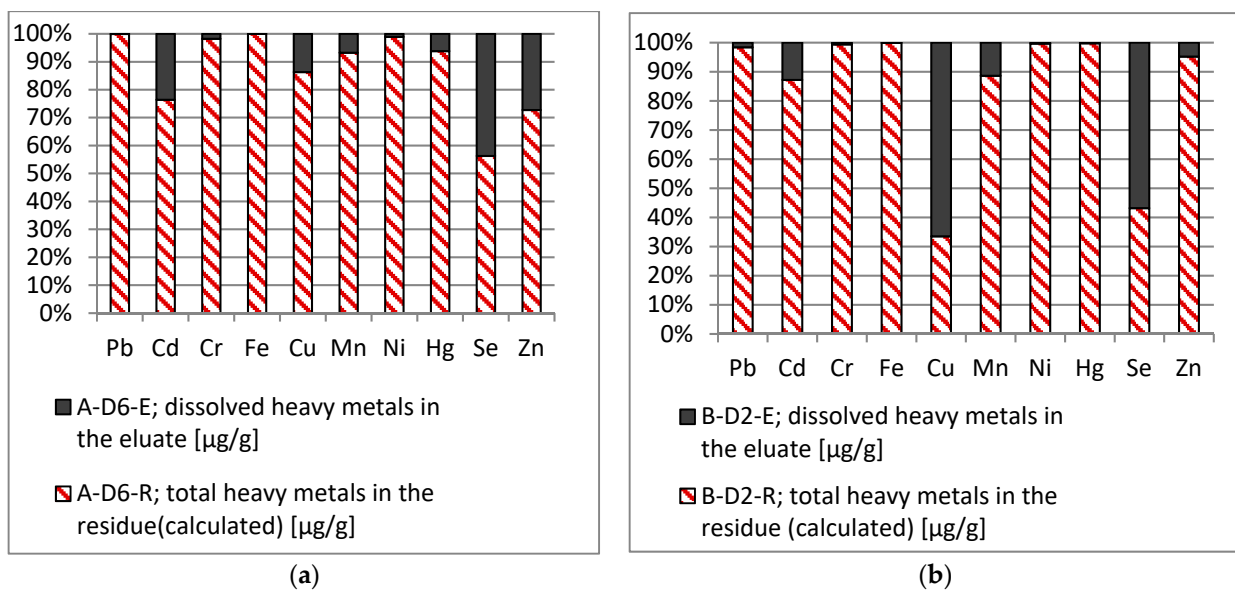
(a)　　　　　　　　　　　　　　　　　　　　　　　　(b)

Figure 4. Comparison of total and dissolved heavy metals of (**a**) dust A-D6 (%) and (**b**) dust B-D2 (%.)

Table 8. Comparison of the emission standards and threshold values with the dust samples.

Parameter	Korea	Japan	China	Austria	Dust Samples
pH	5.8–8.6	6.5–9	5–9	6.5–8.5	8–8.5
TOC (mg/L)	15		<20		15–95
T-N (mg/L)	20	119.6		45	130–203
T-P (mg/L)	1	<14.5	<63		<LOQ–0.53 *
Cr (mg/L)	<2	<2		0.5	0.0022–1.76
Fe (mg/L)	<10	<1		2.0	0.0058–1.25
Zn (mg/L)	5		<4.5	1.0	0.15–7.1
Cd (mg/L)	<0.1			0.1	0.00024–1.22
Hg (mg/L)	<0.005		<0.11	0.005	0.02–13
As (mg/L)	<0.25		<0.011		0.08–0.28
Pb (mg/L)	<0.5			0.5	0.01–3.2
Cu (mg/L)	<3			0.5	0.07–1.2
F (mg/L)	<15	<40		30	56–300
Ni (mg/L)	<3.0				0.0012–0.0052
Mn (mg/L)	<10	<1		<0.9	0.31–4.0

* PO_4-P measured.

4. Conclusions

- The investigations of MEROS dusts taken from two sources, Plants A and B, at different times showed significant differences for Na, K, Cl and SO4 and only low Fe and Zn concentrations. Zn might not influence the process as the addition is low compared to the feed.
- To increase the benefit of reutilization, washing out of the alkalis with water is a possible treatment step to avoid problems in the blast furnace process and to reduce the amount of dust by 90%. However, the comparison with international guidance values indicated that treatment of the remaining wastewater or eluate will be necessary before it can be emitted to surface waters or sewer systems.
- The solid residue can be recycled into the sinter process to reduce potential PCDD/F attached to the activated carbon, as in the sinter process, temperatures of 1200 °C are reached, which are prone to destroying PCDD/Fs.
- With the removal of the soluble fraction, potential precursors for the formation of PCDD/F and PBDD/F such as Cl and Br are also removed from the residue.

- An open question remains regarding the behavior of Hg, as most of the Hg is attached to the solid residue. Additional studies to investigate the benefits are recommended.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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