# Leaching of the residue from the dry off-gas de-dusting and desulfurization process of an iron ore sinter plant

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**Abstract:** The residue from a second-stage dry sinter plant off-gas cleaning process contains both the fine dust from the sinter plant and the sorbent used. Recycling of the material that is usually handled by landfills to the sinter plant feed is not possible because of its chloride content. Leaching of the chlorides allow the recycling of remaining solids. The saline leachate produced contains some heavy metals and must be treated before it is discharged into the sea. In laboratory experiments, leaching tests with the subsequent treatment of the leachate were conducted. After the process was optimized, all heavy-metal concentrations were below the permissible values. The optimum treatment conditions for heavy-metal precipitation were observed to be the filtration of the suspended solids followed by the dosing of liquid with lime milk (pH 10) and the subsequent precipitation using sodium sulfide.

**Keywords:** heavy metals; off-gas cleaning; recycling; residues; leaching; sinter plants

## 1. Introduction

In integrated steel mills, iron ores and fine-grained iron-containing recycling materials are agglomerated in sinter plants. Because of the high volume of off-gas, the sinter plants contribute significantly to the overall atmospheric emissions of steel mills [1]. The off-gas from a sinter plant is usually de-dusted by electrostatic precipitators (EPs) or cyclones, which are installed upstream of the induced-draft fan [2]. To comply with the lower emission limits for dust, $SO_2$, and dioxins, additional emission reduction measures have to be implemented at several sinter plants. Therefore, in the last two decades, a second-stage off-gas cleaning system has been installed at several sinter plants. This additional cleaning stage can be a wet system or a dry system [3–5]. However, the dry systems that use a sorption process for the separation of acid gases and fabric filters for final de-dusting are predominantly used [6–8]. In most of these dry sinter plant off-gas cleaning systems, hydrated lime is used as the reagent to remove the acid components $SO_2$ and HCl [7–11].

For the off-gas cleaning at waste incineration plants, the NEUTREC® process using $NaHCO_3$ as the reagent for acid gases is widely applied [12]. However, this process requires an off-gas temperature greater than 140°C. At sinter plants, the off-gas temperature is often lower than this temperature. An off-gas cleaning process with $NaHCO_3$ is possible at sinter plants only if a reagent recirculation system is used [13].

The dust collected with EPs or cyclones is usually recycled to the feed material in the sinter plant. The residue from a second-stage dry off-gas cleaning process contains larger amounts of sulfate and chloride, which are the result of the separation of sulfur dioxide and hydrogen chloride, respectively, and the collection of the finest dust fraction. Therefore, this residue must be disposed of in landfills [1,14].

To avoid disposal of dry second-stage off-gas cleaning residue by landfill, the leaching of such a residue with water has been investigated [15]. The residue originates from a sinter plant, in which the hydrated lime is used as the reagent for the sorption of acid gases. The yielded material

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can be re-utilized in the cement industry.

Residues from off-gas cleaning systems that use $NaHCO_3$ as the reagent for acid gases can be reused in the production of sodium carbonate [16]. However, the allowable concentrations of Na, K, Cl, $SO_4$, and non-soluble material in the residue are limited.

In this study, a leaching process for the residue from a dry second-stage off-gas cleaning system of a sinter plant where $NaHCO_3$ was used as the reagent for the desulfurization of off-gas was investigated. The solid product left behind after water-leaching is similar to the solid residue from a wet second-stage off-gas cleaning unit because the water-soluble material is dissolved in water in both cases. Therefore, it can be assumed that this material can be recycled to the sinter plant feed in the same way as demonstrated for the residue from a wet second-stage off-gas cleaning system [17–18]. Particular focus was placed on the optimization of the liquid effluent treatment, which should comply with the stringent emission limits. For the removal of heavy metals, various processes are available [19]. The lime-based conventional precipitation, which is used in different variants, is considered to be the most effective means of treating inorganic effluents with higher heavy-metal concentrations [20]. Therefore, this method was chosen in this study for the treatment of liquid effluent.

## 2. Materials and methods

### 2.1. Material

The dust samples were collected from the dry second-stage off-gas cleaning system of an industrial iron ore sinter plant. The first stage of the cleaning system in this plant is an electrostatic precipitator. The dust concentration after the electrostatic precipitator is in the range of 200 mg/m³, and the $SO_2$ concentration is in the range of 700 mg/m³. The second cleaning stage comprises an entrained flow sorption process and a fabric filter. After the second cleaning stage, the concentrations of dust and $SO_2$ are well below the emission limits. In the sorption process, a mixed sorbent consisting of $NaHCO_3$ and lignite coke was used. Part of the residue discharged from the fabric filter was recycled into the sorption process. The three dust samples for the study were taken from the fraction of dust taken to the landfill site.

The following chemicals were used to precipitate heavy metals: lime milk with a concentration of 10wt% $Ca(OH)_2$, 10wt% $Na_2S$ solution, and 15wt% solution of sodium trimercaptotriazine (TMT15). A 15wt% $FeCl_3$ solution was used to remove the excess sulfide after the precipitation

process, and the pH level was adjusted with lime milk or 10wt% HCl.

### 2.2. Leaching and heavy-metal precipitation

The leaching procedure was designed on the basis of the preliminary concept for a full-scale leaching plant. The dust was dosed by a vibration feeder into a plastic beaker containing 1 dm³ of tap water until the chosen liquid/solid (L/S) ratio was reached. The slurry in the beaker was stirred for 10 min at 1000 r/min using an IKA RW20 overhead stirrer with a three-blade propeller stirrer. During another 30 min of stirring, some air was blown into the slurry to oxidize any present sulfite to sulfate. In some tests, the suspended solids were separated by filtration prior to the heavy-metal precipitation phase.

To precipitate the heavy metals, the slurry was stirred in the plastic beaker while the precipitation agent was added. Stirring was continued for another 30 min. In the most of tests, the pH value was adjusted prior to the heavy-metal precipitation phase. In the case where sulfide was used as the precipitation agent, iron chloride was added to precipitate the excess sulfide. For the optimization of treatment process, different precipitation conditions and methods were investigated. Finally, the solids were separated by filtration. Samples of the filtrate were collected for analysis of the heavy-metal concentration.

### 2.3. Chemical analysis

The chemical analyses were conducted as single measurements. All analytical instruments were tested twice a year according to the department's quality standards.

The concentrations of heavy metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn) in the solid samples and in the leaching solutions were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The solid samples were dissolved by microwave-assisted digestion prior to analysis. For the microwave-assisted digestion of solid samples, 6 mL of hydrochloric acid (35wt%) and 2 mL of nitric acid (65wt%) were added to a sample of 0.2 g. The treatment was performed in a START microwave extractor from Mikrowellen–Labor–Systeme (MLS) GmbH; the temperature program was 15 min for heating to 140°C, 15 min at 140°C, and another 15 min for cooling. After cooling, the digested samples were filtered through a fluted filter and diluted with deionized water in a 50-mL volumetric flask. For heavy-metals analysis, a Horiba Jobin Yvon Ultima 2 ICP-OES system was used. The calibration was performed using a multi-element standard (Merck CertiPUR IV) and a single-element standard for As.

Ion chromatography (IC) was used to determine the concentration of the water-soluble ions Na, K, Cl, and $SO_4$ in the solid samples and leaching solutions. Solid samples of approximately 2 g were leached in 200 mL of deionized water for 1 h. To aid the leaching process, the samples were placed in an ultrasonic bath. After the leaching process, the remaining solids were separated by filtration. The chemical analyses were conducted by IC (Dionex ICS-1000 system). The standards for the calibration were prepared by dissolving solid salts in deionized water.

The total carbon content (TC) of residue was determined with a LiquiTOC system from Elementar Analysensysteme GmbH. The carbon was transformed into $CO_2$ by combustion with air, and the $CO_2$ was subsequently analyzed. A Mettler Toledo S40-KS Seven Multi pH meter was used to measure pH levels.

### 2.4. Physical characterization

The particle size distribution of the dust sample was measured using a HELOS laser diffraction instrument with dry sample dispersion from Sympatec. The bulk density of the fly ash samples was determined according to ÖNORM EN ISO 60 [21]. The dry matter content of the filter cake was determined at 105°C using a Sartorius MA35M infrared moisture analyzer.

## 3. Results and discussion

### 3.1. Characterization of the residue

The average concentrations of the main components of three residue samples are shown in Table 1. The high concentrations of sodium and sulfur result from $NaHCO_3$ and desulphurization of off-gas, whereas potassium and chlorine represent the collected fine dust that has passed through the electrostatic precipitator. The contained carbon originates mainly from the lignite coke fraction of the mixed sorbent (95%). The balance is from the carbonate of the unreacted sorbent.

**Table 1.   Composition of the residue**                          wt%

| Component | Average | Standard deviation |
|-----------|---------|--------------------|
| Na | 18.4 | 1.7 |
| K | 15.8 | 2.4 |
| Ca | 0.67 | 0.12 |
| Mg | 0.16 | 0.04 |
| Fe | 1.13 | 0.26 |
| Cl | 17.9 | 2.6 |
| $SO_4$ | 30.9 | 4.5 |
| TC | 6.7 | 1.4 |

The following limits were published by Beck [16] for the utilization of residue in the production of sodium carbonate as: KCl < 15wt%, NaCl > 65wt%, $Na_2SO_4$ < 25wt%, and non-soluble < 0.004wt%. A comparison of these limits with the composition of residue revealed that the investigated residue could not be reused for sodium carbonate production.

The average particle size distribution of residue is shown in Fig. 1. The bimodal distribution is a result of the two main sources for particulate matter: the collected fine dust that has passed the electrostatic precipitator and the used sorbent, which are predominantly contained in the finer fraction and the coarser fraction, respectively. The bulk density of material is 220 kg/m³, which is very low. Therefore, the residue must be mixed with water very carefully to avoid the dust emissions into the air.
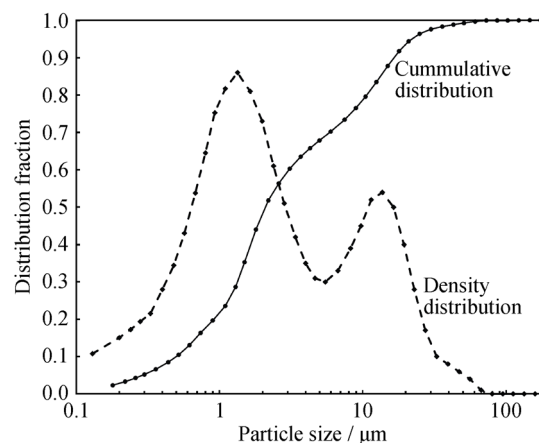


**Fig. 1.    Particle size distribution of the residue.**

### 3.2. Leaching

In principle, a low L/S ratio is preferable because it reduces the amount of fresh water required, the amount of waste water to be treated, and the size of the equipment required. Fig. 2 shows the fractions of dissolved heavy metals as a function of L/S ratio. With the exception of Cu, all of the investigated heavy metals show a decreasing solubility as the L/S ratio decreases. These results can likely be explained by the influence of L/S ratio on the pH value of slurry. A lower L/S ratio results in a higher pH value. In the cases of As and Cr, the dissolved fraction is always less than 0.01.

A L/S ratio of 10 was chosen for the leaching experiments, which was the same as that used by Xu *et al.* [15]. The leaching experiment was conducted five times using different residue samples. The average amount of non-dissolved solids was 13wt% (dry). The composition of leachate,

i.e., the liquid without the suspended solids, is shown in Table 2. The concentration of the soluble salt components (Na, K, Cl, and $SO_4$) is approximately 90 g/dm³. This concentration is approximately three times greater than that of sea water. An environmentally friendly method of disposing of such saline water into the sea is only possible if the concentrations of pollutants are below the permitted limits. In the leachate, the concentration of As is less than the concentration limit. The average Cd concentration is more than 200 times greater than the concentration limit, and the Hg concentration is approximately 40 times greater than the limit. The sum of Cr, Cu, Ni, Pb, and Zn is (4270 ± 2290) µg/dm³, which also exceeds the concentration limit of 800 µg/dm³. Under the assumption that the concentration of leachate equals the average concentration plus three standard deviations, the required reduction efficiencies for Cd, Hg, and the

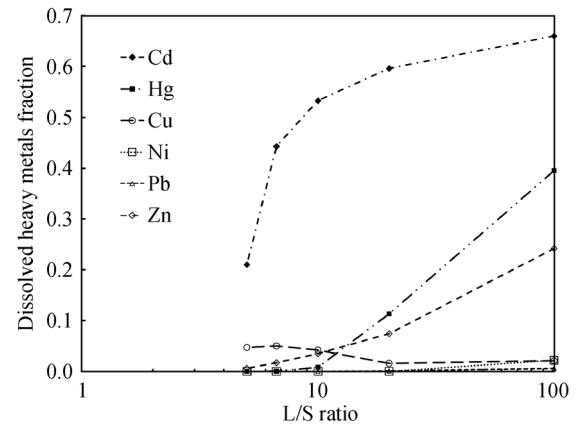sum of Cr, Cu, Ni, Pb, and Zn are 99.7%, 98.7%, and 92.8%, respectively.



**Fig. 2.   Fraction of dissolved heavy metals in relation to the leaching ratio L/S.**

**Table 2.   Composition of leachate**

| Item | Main components / (g·dm⁻³) | | | | Limited components / (µg·dm⁻³) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Na | K | Cl | $SO_4$ | As | Cd | Hg | Cr | Cu | Ni | Pb | Zn |
| Average | 16.7 | 28.2 | 24.2 | 22.0 | < d.l. | 2140 | 200 | < d.l. | 2500 | < d.l. | 200 | 1570 |
| Standard deviation | 1.4 | 2.2 | 0.4 | 0.5 | — | 360 | 60 | — | 1530 | — | 190 | 1020 |

Note: d.l. — detection limit.

### 3.3. Heavy-metal precipitation

A conventional precipitation process was used to precipitate the heavy metals in the liquid effluent. This method was considered to be the most effective means of treating inorganic effluents with a heavy-metal concentration greater

than 1000 mg/dm³ [20]. The target emission limits for heavy metals set by the authorities for an intended pilot plant were comparatively low, as shown in Table 3. Therefore, sodium sulfide was used in a second precipitation stage, which could result in a further reduction of the heavy-metal concentrations [22].

**Table 3.   Heavy metal concentration limits for discharge water** mg/dm³

| Heavy metal | Limit in this study | Ref. [23] | Ref. [24] | Ref. [25] | Ref. [15] |
|---|---|---|---|---|---|
| As | 0.025 | 0.1 | — | 0.01 | — |
| Cd | 0.01 | 0.02 | 0.05 | 0.01 | — |
| Hg | 0.005 | 0.05 | 0.05 | 0.0025 | — |
| Cr | — | 1.0 | 0.5 | 0.1 | 1.5 |
| Cu | — | 1.0 | 0.5 | 0.07 | 0.5 |
| Ni | — | 1.0 | 0.5 | 0.1 | — |
| Pb | — | 0.5 | 0.3 | 0.1 | 1.0 |
| Zn | — | 2.0 | 5.0 | 0.05 | 2.0 |
| Sum of Cr, Cu, Ni, Pb, and Zn | 0.8 | — | — | — | — |

For the optimization of the heavy-metal precipitation process, several different parameters were tested. The addition of lime milk or HCl was used to control the pH value of liquid. In the case of precipitation with $Na_2S$, 2 cm³ of $Na_2S$ was added and the $FeCl_3$ dose was 2.5 cm³. For precipitation with TMT15, 0.65 cm³ of TMT15 was added and the $FeCl_3$

dose was 1.3 cm³. The conditions of tests are summarized in Table 4, together with the resulting reduction efficiencies for the heavy metals whose concentrations exceeded the concentration limit in the untreated leachate. For the required reduction of the sum of Cr, Cu, Ni, Pb, and Zn, the most important parameter was observed to be the liquid pH value.

A pH value of 10 to 10.5 was sufficient in all cases. The filtration of the suspended solids before treatment positively affected the reduction efficiency. In combination with precipitation by TMT15 or $Na_2S$, a lower pH value of 8.5 or 9.5, respectively, was sufficient. For the precipitation of Hg, the filtration of the suspended solids before treatment had little influence. The same result applied to the pH value as long as

the pH value was not less than 4.6. The addition $Na_2S$ or TMT15 appeared to be absolutely necessary for efficient Hg precipitation. The required reduction of the Cd concentration was only possible when the suspended solids were removed from the liquid before treatment. The pH value and the precipitation with sulfides had less impact on the Cd precipitation.

**Table 4.    Treatment processes and resulting reduction efficiency of heavy-metal precipitation**

| Filtration of suspended solids after leaching | pH adjustment agent | pH value | Precipitation agent | Reduction efficiency / % | | |
|---|---|---|---|---|---|---|
| | | | | Cd | Hg | Sum of Cr, Cu, Ni, Pb, and Zn |
| No | — | 8.5 | $Na_2S$ | 81% | **> 99.5%** | 92% |
| No | — | 8.5 | TMT15 | 47% | 81% | 76% |
| No | $Ca(OH)_2$ | 9.5 | — | 96% | — | 87% |
| No | $Ca(OH)_2$ | 10 | — | 97.5% | 60% | **95%** |
| No | $Ca(OH)_2$ | 10.5 | — | 99% | 41% | **96%** |
| No | $Ca(OH)_2$ | 10 | $Na_2S$ | 94% | **> 99.5%** | **99.5%** |
| Yes | — | 8.5 | TMT15 | 99% | **99.2%** | **95%** |
| Yes | HCl | 2.1 | TMT15 | 17% | 97.5% | 38% |
| Yes | HCl | 4.6 | TMT15 | 73% | **99%** | 67% |
| Yes | $Ca(OH)_2$ | 9.5 | $Na_2S$ | 99.1% | 98.5% | **99.5%** |
| Yes | $Ca(OH)_2$ | 10 | $Na_2S$ | **99.7%** | **> 99.5%** | **99.5%** |
| Yes | $Ca(OH)_2$ | 10.5 | $Na_2S$ | **99.7%** | **> 99.5%** | **99.8%** |

Note: data in bold mean that the reduction efficiency is higher than the required efficiency.

As deduced from the experiments, the optimum process conditions of the leachate treatment for heavy-metal precipitation involve the following steps: (1) removal of the remaining suspended solids by filtration; (2) dosing of lime milk to increase the pH value to 10; and (3) precipitation using $Na_2S$ with subsequent addition of $FeCl_3$. According to this procedure, a repetition of the heavy-metal precipitation experiment confirmed the results of the first test. A simplified process flow diagram is shown in Fig. 3. The amount of solids produced in the precipitation step was 2.4wt% (dry). The sum of the remaining solids from leaching and heavy-

metal precipitation for this process was therefore 15.4wt% (dry).

## 4. Conclusions

Direct recycling of the residue from a dry second-stage off-gas cleaning system of a sinter plant to the feed material is not recommended, because most of the chlorine contained in the residue will be released into the off-gas as gaseous KCl and NaCl during the sinter process. During the leaching of residue with water, not only the salts but also some heavy metals are dissolved. Because the concentrations of some heavy metals exceed the allowed concentration limits, the saline solution must be treated before it can be discharged into the sea. The optimum treatment conditions for heavy-metal precipitation are determined to be filtration of the suspended solids, following by a dosing of lime milk to increase the liquid pH value to 10 and the subsequent precipitation using $Na_2S$. The amount of solid remaining after the leaching step is 13wt%. The recycling of this solid residue to the sinter plant feed material can be assumed to be possible because it has been successfully demonstrated for the residue from a wet second-stage off-gas cleaning residue. Therefore, the amount of residue that must be disposed of at
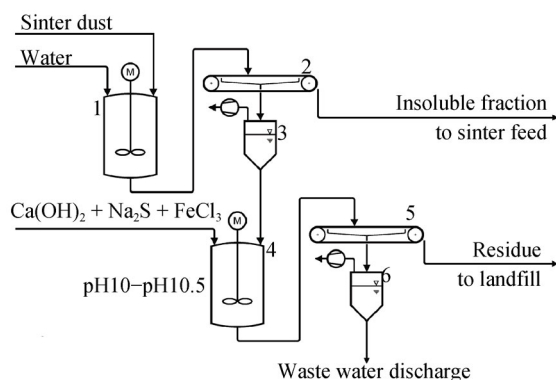


**Fig. 3.    Simplified process flow diagram.**

landfill sites can be reduced to about 2.4wt% based on the original amount of residue.

## Acknowledgements

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