

Fine-Particle Characterization— An Important Recycling Tool

Bo Lindblom, Caisa Samuelsson, Åke Sandström, and Guozhu Ye

This paper summarizes the results from different research projects on fine-particle characterization of metallurgical residues, such as hydroxide sludge, electric-arc furnace dust, and copper-converter dust. These studies demonstrated that characterization is essential for developing new recycling strategies. The basic knowledge of the chemical and physical properties of the residues obtained by the characterizations also provides necessary information on potential problems that could be encountered during the processing of such materials.

INTRODUCTION

In the metallurgical industry, residues such as dusts and sludges are generated in various amounts and compositions. Demands from society and governmental legislation have applied pressure on the industry to minimize the amount of waste to be landfilled and to find solutions for the recovery of the generated residues. Depending on the chemical and physical properties of the materials, they can be recycled within the plant, externally treated for recovery of metals, or deposited in a landfill. Another option is to make use of the residues in other products. The characteristics of the residue—composition, particle size, water content, oil content, or other impurities—can restrict the recycling from a technical, economical, or environmental point of view. A basic knowledge of the chemical and physical properties of the residues is of fundamental importance to propose the best recycling option. This paper summarizes research projects on the characterization of fine-particle residues that were performed by MIMER, the Minerals and Metals Recycling Research Centre at Luleå University of Technology in

Sweden, and MEFOS, the Foundation for Metallurgical Research, also in Sweden, in recent years.

HYDROXIDE SLUDGE FROM STAINLESS-STEEL PRODUCTION

The characterization of pickling sludges from two stainless-steel companies was carried out using chemical analysis, x-ray-diffraction analysis (XRD), particle-size distribution, scanning-electron microscopy (SEM), and thermogravimetric analysis (TG).¹ In addition, some solid-state reduction products were characterized. The chemical composition of a typical hydroxide sludge is (wt.%): Fe 13%, Cr 3%, Ni 3%, F 15%, S 3%, and Ca 21%, with a dry substance content of 37%. The relatively high sulfur content in this sludge arises because the pickling acid is mixed with a neolyte (Na_2SO_4) bleed and wash water in the neutralization plant.

The original filter cakes consisted of a very fine-grained material with a mean particle size of about 3.7 μm . X-ray-diffraction analysis revealed that the filter cakes were amorphous and SEM studies showed that the elements Fe, Ni, Cr, F, and Ca were evenly distributed among the particles. These properties make it impossible to utilize physical methods

such as magnetic separation or flotation techniques to upgrade the hydroxide sludge. To study the effect of heating on the sludge, a stepwise heating in air up to 900°C was performed. X-ray-diffraction analysis showed that several crystalline phases, such as CaF_2 , and spinels of Fe-Ni-Cr composition were formed. The thermogravimetric curves of two dried filter cakes are given in Figure 1. For both the sludges, the weight loss starts at approximately 120°C with the highest rate at about 250°C. The weight loss becomes much less at about 750–1,250°C. The total weight loss for these two samples was 10.5% and 14.2% between 120°C and 1,000°C. The weight loss in the temperature range 120–600°C is mainly caused by evaporation of hydration water in the sludge. This information is important for the selection of proper agglomeration techniques and for the prevention of cracking in the agglomerates during heating. An XRD examination on the products from the solid-state reduction of pickling sludge with petroleum coke found that metal phases form even at 800°C; however, to reduce all metal-oxide spinels, a heating temperature of 1,200°C is required. This result is consistent with the data obtained from both the thermodynamic calculations and the previous thermal analysis tests. To make the hydroxide sludge suitable for recycling into an electric arc furnace (EAF), a pre-reduction process is needed. This process, however, has to be optimized to ensure that the spinel-phases NiFe_2O_4 and FeCr_2O_4 are completely eliminated. In a sample reduced at 1,200°C, metallic Fe is combined with metallic Ni and Cr forming solid solutions such as FeNi and FeCrNi. Some particles contain CaS and CaF_2 . The relatively high sulfur content in the sludge will cause recycling problems

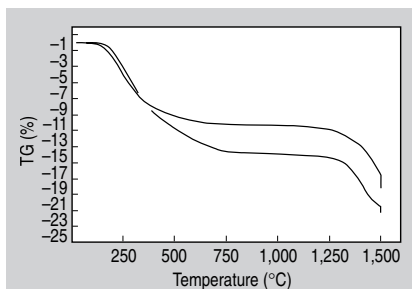


Figure 1. The thermogravimetric curves for two hydroxide sludges.

because many unit operations in stainless-steel making are sensitive to sulfur contamination. In this case, the best way to avoid sulfur would be to avoid mixing the solutions from the pickling bath and the neolyte tank in the neutralization plant; these solutions have to be treated separately. Sample reduction studies also found that the particle sizes of the reduced product are considerably larger than those in the original filter cakes and may facilitate a physical separation of the metal alloy. If the sulfur has been removed prior to reduction, it might also be possible to utilize the non-metallic part as flux in the steel-making process.

CHARACTERIZATION OF EAF DUST

Electric-arc furnace dust from a scrap-based steel mill in Sweden was characterized to study its suitability for a proposed hydrochloric acid leaching process. In this process, the dust is leached in HCl media to extract a pure zinc-oxide product and to recycle the leaching residue to the EAF.^{2,3} Impurity elements, such as lead and copper, must be recovered separately, for example through cementation. To develop such a process, it is important to quantify the leachable and non-leachable parts of the dust and the impurity species in the final zinc-oxide product. Characterization of the EAF dust was carried out using a combination of standard analytical techniques as well as leaching experiments. Chemical analysis obtained by inductively coupled plasma mass spectroscopy (ICP-MS) and XRD gave the following results: the main elements

Phase	Zinc-Oxide Fume						
	EAF Dust		Before Leaching			After Leaching	
	XRD	SEM	XRD	SEM	TEM	XRD	TEM
NaCl	X	—	X	—	—	—	—
KCl	X	X	X	X	X	—	—
CaF ₂	—	—	—	—	—	—	X
Cl-silicate	—	—	—	—	—	—	X
ZnO _{free}	X	X	X	X	X	X	X
ZnO-Fe ₂ O ₃	X	X	—	—	—	—	—

were (wt.%) Zn 21.9%, Fe 29.6%, Mn 2.7%, Pb 0.7%, Cu 0.2%, Cr 0.7%, Ca 9.1%, and Mg 0.7%, and the main crystalline phases were spinels (unleachable), ZnO, CaO, and Ca₂Fe₂O₅ (leachable) (Figure 2). The relatively high calcium content in the dust is undesirable because it may cause excessive acid consumption in the leaching process. The particle-size analysis revealed a fine dust with a d₉₀ of 14 μm and a median size of 2 μm. This fine-particle size is favorable for fast leaching kinetics, but can complicate the filtration of the leach residue. Scanning-electron microscopy and electron-microprobe analyses were employed in order to study the distribution of Fe, Zn, O, Ca, and Mn in the particles. Some particles containing Ca/O and Zn/O can be easily identified, whereas the majority of the particles contains the elements Fe/Zn/Mn/O, indicating the presence of ferritic spinels forming solid-solution phases according to the general formula (Mn_xZn_yFe_{1-x-y})Fe₂O₄.

The amount of the leachable phases was determined by a series of leaching

tests with hydrochloric acid at two different conditions: pH = 7 at 25°C and pH = 3 at 80°C. It was found that 37% of the total calcium is free lime, leachable at pH = 7, and 51% is calcium ferrite, leachable at pH = 3. The remaining 12% of the calcium is bound in another non-soluble form, probably a slag phase. This means that as much as 88% of the calcium content in the dust will be dissolved in a leaching process. Furthermore, it was found that 63% of the zinc, as zinc oxide, was leachable at pH = 3, and subsequently can be recovered as a valuable zinc product. It should be mentioned that 20% of the manganese was dissolved. The only leachable manganese-oxide species under the leaching conditions applied is MnO. Thermal analyses were carried out in air and argon atmospheres in the temperature range 25–1,200°C. Under oxidizing conditions, an exothermic transition was observed at 450–650°C with a mass increase of 0.6% as shown in Figure 3. This was interpreted as the oxidation of a solid compound, probably MnO. Leaching at pH = 3 also dissolved 54% Pb, 27% Cu, 2% Cr, and 40% Mg. Only spinel phases were present in the final leach residue (see Figure 2).

In brief, the compositions of the EAF dust are variable and complex; some particles are homogeneous containing a single oxide, but the majority of the particles are polymetallic oxides. The most common oxides in the dust belong to the spinel group and are made up of solid solutions of the pure compounds ZnFe₂O₄, MnFe₂O₄, and Fe₃O₄. The results suggest that a process consisting of leaching of the zinc followed by treatment of the iron-enriched residue in an EAF is a way to recycle this EAF dust. However, the relatively high lime content makes acid leaching of this type

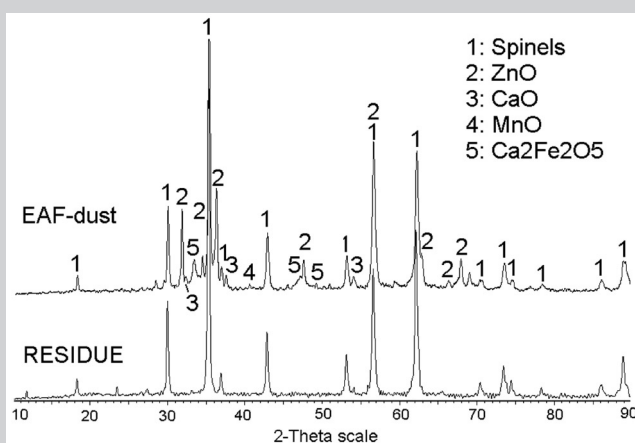


Figure 2. An X-ray diffraction pattern of EAF dust and residue after leaching (pH = 3).

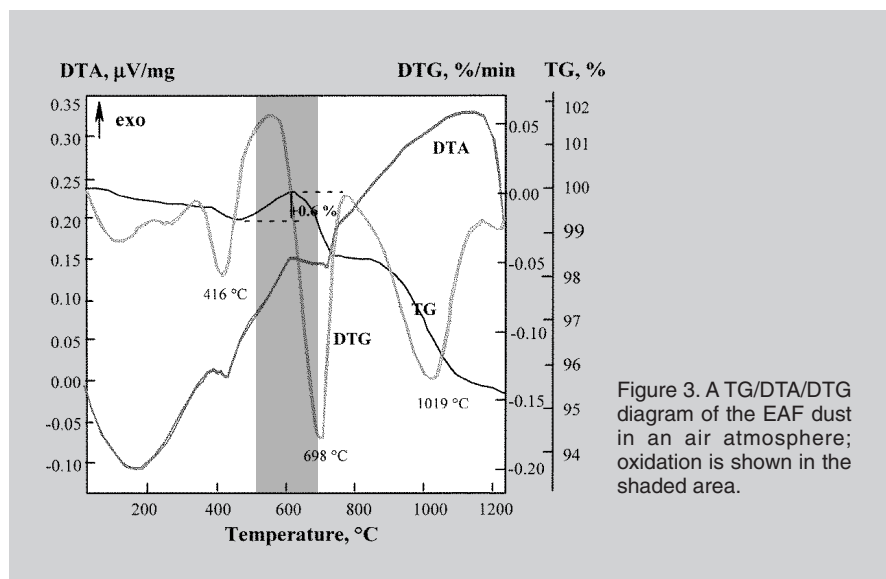


Figure 3. A TG/DTA/DTG diagram of the EAF dust in an air atmosphere; oxidation is shown in the shaded area.

of dust less attractive because of excessive acid consumption; consequently, measures should be taken in the EAF operation to reduce the lime content of such dusts. Also, care has to be taken to avoid manganese in the leaching solution because it decreases the economical value of the final zinc-oxide product. Finally, the leaching conditions must be optimized in order to avoid the accumulation of impurity elements such as lead and copper in a large-scale recycling process.

CHARACTERIZATION OF HALOGEN-BEARING PHASES

Electric-arc furnace dust was treated in a direct-current arc furnace at 1,500°C to produce a ZnO-enriched product for electrolytic zinc recovery in a conventional sulfuric-acid based operation. The ZnO-enriched products consist of 80–85% ZnO, 5–10% PbO, 5–8% halogens, and 2% others. After water washing, the total halogen content was reduced to 200 ppm. However, the maximum level for the total chlorine and fluorine content in the ZnO-enriched product allowed for such application

was limited to 100 ppm. To find a method for lowering the halogen content to the acceptable level, a comprehensive characterization study on the EAF dust, the ZnO-enriched product, before and after water washing was performed.⁴ Table I shows that most of the halogen-bearing phases in the EAF dust and the ZnO product are mainly soluble NaCl and KCl. The minor unleachable amount of halogens in the leached ZnO product occurs as CaF₂ and an aluminate-silicate phase that contains up to 10% chlorine. These two halogen-bearing phases originated from the carry-over of unreacted EAF dust. The lowest possible halogen content in the obtained ZnO product depends, thus, on the amount of the carry-over dust that again is dependent on the stability of the process and the operation conditions. The total content of chlorine and fluorine in the residue after water washing could be further reduced from 200 ppm to 50–100 ppm by soda washing.

CHARACTERIZATION OF COPPER CONVERTER DUST

The gas stream from the copper converter passes through four main parts

in the gas-cleaning system: a settling chamber, a waste heat boiler, a cooling tower, and an electrostatic precipitator (ESP). The copper converter dust is carried through the gas-cleaning system and can be found at different locations in various amounts and compositions. Dust samples from the gas-cleaning system were collected and characterized using chemical analysis, microprobe equipment, and XRD.⁵

Part of the collected dust originates from slag particles (FeO-silicates), matte particles (Cu-Fe-sulfide), and SiO₂ (i.e., from mechanically formed dust). However, a large fraction of the dust is formed by vaporization of metal compounds from the melt (e.g., Pb, Zn, As, Bi, Sb compounds, followed by condensation at decreasing temperatures in the gas-cleaning system—the chemically formed dust). A large part of the coarse mechanical dust is deposited early in the gas-cleaning system, in the settling chamber and waste heat boiler. The chemically formed dust, which has a smaller particle size, is transported a longer distance and is largely collected in the ESP. This can be seen in Table II, which shows that the Cu and SiO₂ contents of the dust decrease while the contents of Pb, Zn, As, Sb, Cd, and Bi increase with increasing distance from the converter. The microprobe analysis of the settling-chamber dust (Figure 4a) shows that the dust consists mainly of irregularly shaped slag particles (SiO₂) with a particle size up to 1,000 μm and spherical matte particles (Cu-Fe-S) with a diameter of up to 300 μm. The matte particles from the settling chamber generally contain line-shaped inclusions of PbS. Inclusions of iron oxide were also seen in matte particles. Slag particles containing mainly iron oxide and silica with minor amounts of zinc and lead are present. The fine-particle fraction observed in the sample contains mainly

Table II. Chemical Composition of Dust Samples Collected from the Copper Converter Gas-Cleaning System*

	Fe	Cu	Zn	As	Cd	Sb	Pb	Bi	S	SiO ₂
Settling chamber	3.0	25.8	1.7	0.25	0.07	0.05	3.8	0.08	8.0	30.6
Waste heat boiler	2.3	21.8	4.7	1.1	0.4	0.1	14.8	0.5	10.3	37.9
Gas pipe	2.8	25.2	4.4	1.1	0.3	0.1	13.0	0.4	10.5	20.5
Cooling tower	2.9	21.5	6.4	1.7	0.4	0.1	16.4	0.5	12.2	15.4
ESP	0.2	0.8	9.6	6.6	1.1	0.3	41.8	1.4	9.4	0.7

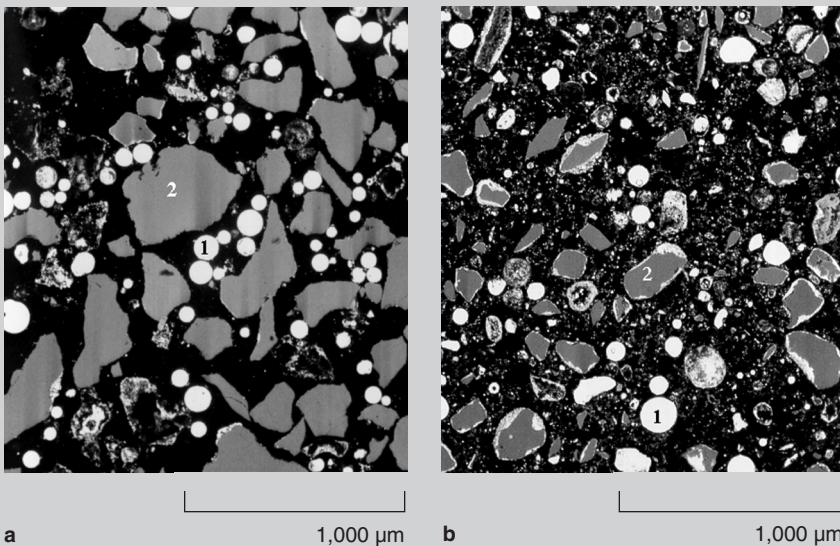


Figure 4. Microprobe images of dust collected during the slag-making stage in (a) the settling chamber and (b) the cooling tower. The images show (1)—copper-sulfide particles, (2)—silica-particles, and fine chemically formed dust particles present as a rim around matte and silica particles.

lead and zinc, with a particle size of approximately 1 µm.

The dust sample from the cooling tower (Figure 4b) has a composition similar to that of the dust from the settling chamber, but significant differences exist. The cooling-tower dust contains a larger proportion of the very fine-grained material that contains mainly lead and zinc as compared to the settling-chamber dust. Even the coarser particles are smaller than those from the settling chamber. The slag particles have a size of up to 300 µm, and the matte particles have diameters of up to 150 µm. Inclusions of copper oxide are found in the slag particles from the cooling tower. It can be seen in the samples from both the settling chamber and the cooling tower that the very fine-grained particles form larger agglomerates and coat the surfaces of the silica particles, in particular, but to some extent also the copper-sulfide particles. X-ray diffraction analysis indicates that the dust from the settling chamber contains SiO_2 , CuFeS_2 , Cu_{2-y}S , PbSO_4 , and trace amounts of Fe_2O_3 and Fe_{1-x}S ; the dust from the cooling tower contains

SiO_2 , Cu_{2-y}S , $\text{CuO}\cdot\text{CuSO}_4$, PbSO_4 , FeS_2 , and trace amounts of CuFe_2S_3 , Fe_2O_3 , and Fe_3O_4 .

A selective separation of the mechanical and chemical dust in the converter gas-cleaning system was observed; the separation was caused by the difference in particle sizes. However, part of the fine material forms larger agglomerates and clusters around larger slag and matte particles, a fact which will somewhat limit their separation. Further studies⁶ indicate that to obtain selectivity in the condensation of metal compounds, such as lead and zinc, gas cleaning at high temperatures is required.

CONCLUSIONS

Characterization is of essential importance for new recycling strategies; characterization studies provide the necessary information on the possibilities and potential problems of processing such materials. For example, the study on hydroxide sludges has resulted in a decision on the separate storage of the pickling effluent, thus eliminating the sulfur-contamination problem. The sulfur-free oxide sludge could thus

be used directly in the steel-making processes. The EAF dust study revealed the importance of good furnace operation. Improper addition of lime to the EAF results in a low yield of lime and a poor quality of EAF dust because much of the added lime ends up in the EAF dust directly. Poor operation of the EAF dust-treatment process will result in a higher dust carry-over with a consequential reduction in the quality of the ZnO product. A separation of the chemically and mechanically formed dust particles was observed in the copper converter circuit, resulting from the difference in particle sizes. Further separation of the copper converter dust into fractions with enriched metal contents is possible by applying a high-temperature gas filtration system.

References

1. B. Lindblom and P. Ma, "Characterization and Reduction Studies of the Waste Pickling Sludge of Stainless Steel," *REWAS '99*, Vol. 2, ed. I. Gaballah, J. Hager, and R. Solozabal (Warrendale, PA: TMS, 1999), pp. 1493–1501.
2. N. Kanari et al., "New Process for the Treatment of EAF Dust," *Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects*, Vol. 2, ed. B. Björkman, C. Samuelsson, and J.-O. Wikström (Luleå, Sweden: Luleå University of Technology, 2002), pp. 221–230.
3. N. Menad, Å. Sandström, and B. Lindblom, "Characterization of Dusts Generated from Metallurgical Processes," *Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects*, Vol. 2, ed. B. Björkman, C. Samuelsson, and J.-O. Wikström (Luleå, Sweden: Luleå University of Technology, 2002), pp. 639–649.
4. Guozhu Ye, J. White, and Liu-Ying Wei, "Association of Halogens in Electric Arc Furnace Dust and Zinc Oxide Fume before and after Leaching," *REWAS '99*, ed. I. Gaballah, J. Hager, and R. Solozabal (Warrendale, PA: TMS, 1999), pp. 1503–1510.
5. C. Samuelsson and B. Björkman, "Dust Forming Mechanisms in the Gas Cleaning System after the Copper Converting Process, (I) Sampling and Characterisation," *Scand. J. Met.*, 27 (1998), pp. 4–63.
6. C. Samuelsson and B. Björkman, "Dust Forming Mechanisms in the Gas Cleaning System after the Copper Converting Process, (II) Thermodynamic Studies," *Scand. J. Met.*, 27 (1998), pp. 64–72.

Bo Lindblom and C. Samuelsson are senior research metallurgists and Åke Sandström is a lecturer at Luleå University of Technology, Luleå, Sweden. Guozhu Ye is a senior researcher at MEFOS, Luleå, Sweden.

For more information, contact Bo Lindblom, Luleå University of Technology, Division of Process Metallurgy, SE-971 87 Luleå, Sweden; e-mail Bo.Lindblom@km.luth.se.