

Recycling of EAF dust by semi-continuous high kinetic process

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The horizontal high energy rotor ball mill (Simoloyer®) is used to break and activate dry solids. It is used for dry-milling and in the vertical mount for wet-milling in leaching processes. Technical electric arc furnace (EAF) dust with high contents of zinc oxide, zinc ferrite and magnetite is efficiently separated by ambient temperature leaching. The process shows promise for industrial application.

Electric arc furnace (EAF) dust is being generated as waste product from the process of steel manufacturing and super large volumes of EAF dust are produced in every industrialized country. The record for Germany in 1996 gave about 199,577 tons of EAF dust and for US 768,639 tons [1]. EAF dust causes environmental problems and requires special care for handling and final disposal.

Aside from landfill deposition this dust is up to now treated by the pyro-metallurgical "hot" recycling process (at least in Europe), by which lead, cadmium, and zinc are volatilized or boiled out from the melt and then re-condensed and collected in the exhaust system. The

collected cake is then used by zinc manufacturers as feed stock material for the production of pure zinc, lead and cadmium. The remaining inert material (slag) has still a high iron concentration and significant

remnants of zinc and lead, which contains average wt-fractions of metals and their oxides such as 25% Zn, 25% Fe, 5% Pb, some Sn, Cd, Cr and Cu.

Because of the high energy consumption, a high remaining slag share of approx. 70%, and the risk of "dioxine"-emission, the hot process does not play an important role from the economical and environmental aspect and most of the EAF dust is disposed in hazardous waste landfills and "buried" at costs as high as EUR 150-200 per ton. Since environmental regulations become more and more tight and significant change is announced for the near future, there is a high motivation to find alternative economical and environmentally friendly routes such as recycling processes that are operated at low temperature ("cold" processes).

The topic of "cold" recycling of EAF dust is not new and more than 40 reports can be found in the literature. However, all of them end in similar difficulties described by an insufficient leaching process due to a very low percentage of the leaching yield when stirring or low kinetic milling processes are used.

What has not been done now is the application of High Kinetic Processing (HGP) which provides a reactive milling operation with high kinetic energy impact at relative velocities of the grinding media up to 14 m/s



Fig. 2: horizontal rotary ball mill (Simoloyer® CM01-21) with air-lock for loading, operation and unloading under vacuum and/or inert-gas.

in a closed and continuous gas-circuit system.

The present paper describes initial activation tests where a laboratory scale (2 l) High-Energy-(ball)-Mill (Simoloyer) was used to activate the EAF dust leaching. This new method is expected to lead to an economic and environmentally friendly way of recycling and decontaminating of EAF dust and furthermore, to extract useful materials from the dust.

Experimental Design

Fig. 1 shows the flow chart of the recycling process for EAF dust. The dust from the electric arc furnace was treated by a horizontal rotor high energy ball mill, the Simoloyer (Fig. 2). During this High Energy Milling (HEM) process on the one hand the particle size of EAF dust

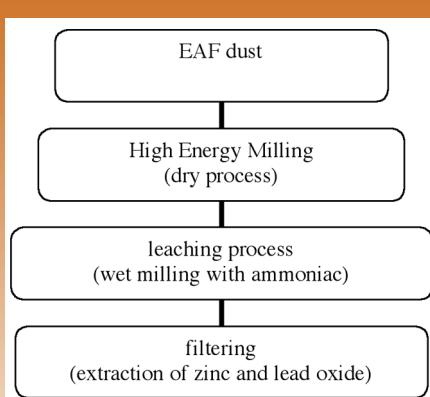


Fig. 1: Previous flow chart of the recycling

was reduced down to about 1 µm, and on the other hand the as-milled EAF dust was highly activated due to a strong mechanical impact from the fast flying milling balls (up to 14 m/s), e. g. deformation, breaking and cold welding of the powder, which caused a lot of structure defects of EAF dust and leads to an increased activity of the dust.

The leaching process was then performed with the same mill, but in the vertical mount (Fig. 3) and under wet condition. The vessel was filled with the balls, the substrate and the leaching solution. The rotor speed was the same as in the dry-milling. The solids and solutions were separated by centrifugation.

Clearly, the HEM process could also be carried out continuously for large scale production. Fig. 4 shows a laboratory device for continuous or semi-continuous (auto-batch) operation. This unit is based on a closed carrier-gas system driven by a side-channel-turbine adapted to a Simoloyer CM01-2ls1 with 2 cyclones for separation/classification, some valves for circuit-control, rotary vane feeders with air-locks, filter, evacuation pump, computer- and electrical control, a special separation and other units.

Milling Device

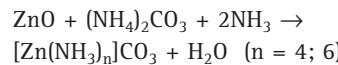
The horizontal high energy ball mills are known from academic and industrial applications in Mechanical Alloying (MA) [2-6], High Energy Milling (HEM) [7] and Reactive Milling (RM) [8]. They supply the highest relative velocity of grinding media, which leads to a high level of kinetic energy transfer, an intensive grinding effect and short processing times. The contamination of the processed powders by the milling tools is naturally lower since the process is based on the collision of grinding media rather than on shear and friction interaction of the same which usually leads to higher abrasion. The systems are presently available from 0.5 to 400 liter grinding chamber capacity [9] where larger volumes seem to be possible.

Experimental

A dry EAF dust sample of Georgsmarienhütte (grain size ca. 5 µm) contained 33.4% Zn, 27.5% Fe and 1.5% Pb according to AAS (HNO_3 pressure decomposition). Further constituents are minor quantities of light and heavy atom oxides and silicates. 200 g of the dust were milled down to about 1 µm size in the horizontal 2 l Simoloyer for 20 min at 1300 rpm with 2 kg steel balls of 3 mm diameter while cooling with tap water of 14 °C. The vertical leaching was performed under the same conditions after addition of 1.2 l of the leaching solution. The leaching solution was prepared from 590 ml of 25% NH_3 , 610 g $(\text{NH}_4)_2\text{CO}_3$ and 800 ml water to dissolve the salt. Alternatively, 590 ml 13.4% NH_3 instead of 25% NH_3 and un-milled EAF dust were used. The zinc, iron and lead contents were detected by AAS.

Results

While the eventually pre-milled industrial waste material is effectively leached from ZnO and PbO by efficient milling at room temperature in one step, previous experiments using attritor techniques were incomplete and required a second leaching at elevated temperature. The initial goal was to separate zinc and lead for further use, without destroying the iron oxide matrix that shall be recycled for steel production. The easiest way with technical potential is the leaching with ammonia and ammonium carbonate which dissolves zinc oxide (ZnO) and lead oxide (PbO) according to the formula (the index n depends on the ammonia concentration):



Franklinite (zinc ferrite, zinc spinel, zinc iron oxide, ZnFe_2O_4) is an important constituent of the dust in question which cannot be leached with ammonia because it does not dissolve neither at room temperature



Fig. 3: Simoloyer® CM01-2l in vertical mount for the leaching process

nor at 200° - 250° C in an autoclave (<10 % dissolved). Even HEM does not help in breaking the resistance of zinc ferrite against that leaching reagent. The separation of ZnO and ZnFe_2O_4 by ammoniacal leaching has been described [10]. The experimental design had to be changed into separation of leachable zinc and lead (they can be separated by selective precipitation of their carbonates), iron from its oxides (magnetite, Fe_3O_4) and zinc ferrite (ZnFe_2O_4) in cold one-step processes. The leaching vertical ball-milling was performed for 10, 20, 30 and 60 min in order to assess the efficiency. It turned out that the wet-milling efficiency with the higher concentrated solution was so good that the 10 min runs both with pre-milled (1 µm) and original material (5 µm) were complete and longer milling was unnecessary. The longer milling under the corresponding conditions gave the same AAS result throughout. All of the leachable Zn and the lead from 200 g EAF dust were in solution that contained the equivalent of 55.76 g ZnO and 6.64 g addi-

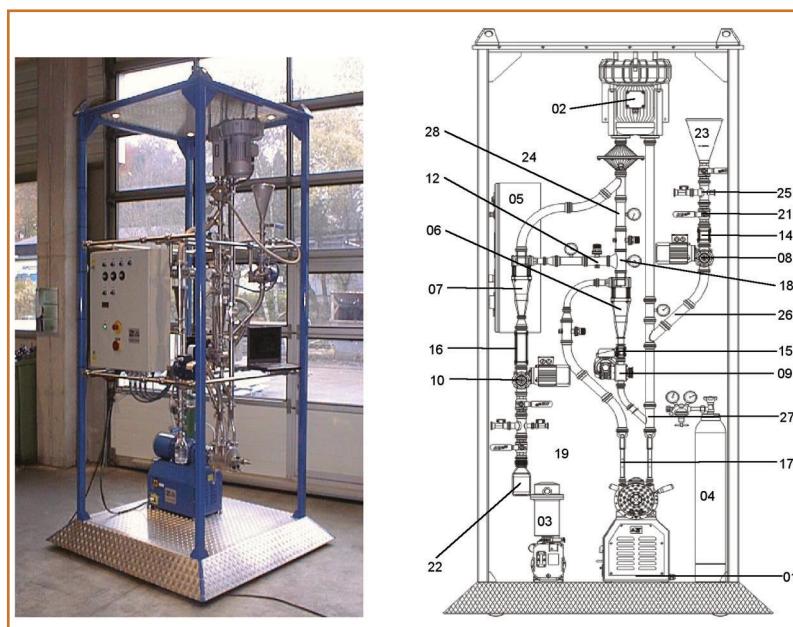


Fig. 4: Pilot-set-up of a high energy ball mill (Simoloyer® VS01a) with air/inert carrier gas-cycle and powder separation/classification system.

ID	unit	Function
01	Simoloyer CM01-s1	High Kinetic Processing
02	side-channel-turbine SKV180a-DN40	carrier gas drive
03	vacuum pump DUO 10	air-lock operation
04	gas-bottle 10 liter	Gas supply internal & air-lock
05	electronic cabinet	additional Maltoz-support, control of pump, rotary vane feeders & carrier gas drive
06	laboratory cyclone ZK70-L (a)	separation of heavy particles in primary circuit
07	laboratory cyclone ZK70-L (b)	separation of all particles in secondary circuit
08	rotary vane feeder ZS40m (a)	pressure compensation supply in injection device
09	rotary vane feeder ZS25m	pressure compensation supply in bypass cyclone (a)
10	rotary vane feeder ZS40m (b)	pressure compensation supply at product port
11-13	butterfly valve KV-DN40	velocity control of multiphase-flow in primary- and secondary circuit
14	transparent pipe module GR-DN40x100	visual control of injection process of starting powder
15	transparent pipe module GR-DN25x75	visual control of separation process at cyclone (a)
16	transparent pipe module GR-DN40x200	visual control of feed-rate at ZS40m (b) at product port
17	pipe switch RW40-16-A	transfer of multiphase-flow in and out of grinding unit W01-s1
18	KF-space-switch RW40-B	separation in multiphase-flow
19	pipe bends RBA-DN40 & DN25	transfer of multiphase-flow in primary- and secondary circuit
20	adapter KF-A	transfer of multiphase-flow in primary- and secondary circuit
21	valve adapter DN*G*DN*	transfer of multiphase-flow in primary- and secondary circuit
22	KF-glass-container DN40-G1-500 cc	display-container for product after air-lock out
23	KF-valve-container DN40-G1-21	container for starting powder or granules before air-lock in
24	vacuum screen unit VSK28	protection-filter for carrier gas drive
25	KF-calming pipes	cross-tube for air-lock evacuation and gas-supply
26	KF-tubes, straight	adaptation of measurement sensors and gas-supply
27	KF-junction-tubes	flow switch, bypass and injection
28	pressure-gauge DMD16	record of flow-parameters

tional oxides (silicates) including the lead from 3.36 g PbO. Importantly, the difference between pre-milled and un-milled EAF dust showed up if the ammonia concentration was decreased (13.4% NH₃ instead of 25% NH₃). The benefit of the pre-milling (which will be more important with larger grain sizes) could be clearly demonstrated: complete leaching of ZnO from pre-milled dust required 30 min as compared to the untreated dust that was “complete” after > 60 min.

The centrifuged washed and dried residue of the “complete” ammonia leachings (137.6 g) contained 16.0% Zn in the form of 81.2 g zinc ferrite and an additional quantity of Fe in the form of 24.0 g magnetite. The previous wet-milling was so efficient that all of the magnetite and further impurities (31.7 g) could be dissolved by 2n-HCl in 1 h at ambient temperature upon standing. The centrifuged and dried residue yielded 81.9 g (analytically expected 81.2 g) of highly pure zinc ferrite in the form of about 1 µm sized uniform particles that may be a valuable and useful product. XPR-analysis gave the characteristic lines of ZnFe₂O₄. Therefore, the aims of low temperature leaching were achieved at low energy costs.

Conversely, the difficulties with previous attritor techniques (stirring among the balls) and low kinetic milling are evident from the requirement of using pre-milled dust, 2 h leaching time at 2500 rpm and 50° C, as well as the necessity of a second leaching at 80° C, both with the higher concentrated leaching solution in order to dissolve all of the leachable zinc. Other techniques such as high temperature acidic leaching do not isolate the zinc ferrite but provide solutions that contain both the zinc and the iron which are laboriously separated [11, 12].

Conclusion

We have shown that efficient wet-milling with the large scale vertical Simoloyer ball mill is feasible for industrial-scale leaching and that

the leaching reagents have to be carefully selected. Clearly, for leaching zinc ferrite in matrices that are higher in Fe_3O_4 content, different leaching reagents will have to be developed that do not have the disadvantages of the known reductive, acidic (hot acid), and metal ion exchange (by FeSO_4 or FeCl_3) techniques which are available from the (patent) literature. Clearly, the leaching with the vertical Simoloyer will be usable for other hydrometallurgical leaching processes, in combination with horizontal dry-milling for selective leaching of ores at low temperatures. These low cost processes are environmentally friendly.

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