The DK process – for the recovery of iron and zinc from BOF dusts and sludges

The DK process uses a blast furnace to treat 450kt/y of iron and zinc containing residues from the European iron and steel industry. DK is the only producer of hematite pig iron in Western Europe with an annual production of 280kt and also produces a zinc concentrate.

By Dr Karl-Josef Sassen* & Dr-Ing Carsten Hillmann**

DK was founded 135 years ago as Duisburger Kupferhütte. Its aim at that time was to purchase large amounts of pyrite on the world market for the manufacture of sulphuric acid. After roasting the pyrite, DK recovered nearly every chemical element from the cinders – for example iron, copper, zinc, cadmium and even silver and gold.

With changing methods of sulphuric acid manufacture and an extremely complex and expensive process, the then owner, Rio Tinto Zinc, decided to close the plant in 1983. Due to the legal requirement to clean up the site, RTZ installed a trust to continue operations to process the remaining cinders on site. While doing so, more industrial wastes were added to the raw material mix and it became evident that the process could be operated using only industrial wastes.

In 1991 DK was renamed DK Recycling und Roheisen GmbH to give expression to what the company does: recycling of wastes and production of pig iron.

The company still belongs to a trust, meaning that the employees own the company. The actual number of employees is about 250.

Situation on residues

Much effort has been made by the steel industry to recycle as much iron residues as possible. The balance from the German steel industry in 2006 shows that 72% of iron and steelmaking dusts are recycled, but still some 300kt/y of BOF dusts and sludges as well as BF sludge go to internal or external dumps (**Fig 1**).

A similar situation is found in other European steel industries which makes DK, with its location Duisburg in the middle of Western Europe, an ideal location to receive dusts to treat from across Europe.

DK presently processes 460kt/y of material from nine different steelworks from six European countries together producing some 77Mt of crude steel.

Raw material for DK

BOF dust is the dominating portion in the raw material mix accounting for 52.5% of the input (**Fig 2**). Sand is used to adjust the basicity and small amounts of iron ore are added to supply some coarse particles to the mix to improve permeability.

BOF dusts have a high iron content and generally few detrimental elements, but there are BOF dusts with extremely high zinc contents as well as blast furnace (BF) sludges with high carbon contents (**Table 1**). Besides some difficult chemical compositions, the moisture content also varies between zero and 40% causing some difficulties.

Sinter plant

Other than that in a regular sinter plant, DK has no blending bed. Mixing of the raw materials is by a grab crane. After mixing, the crane feeds several bins under which runs a feed belt and weighers to compose the material blend (**Fig 3**).

Another difference compared to a regular sinter plant is that cooling of the sinter is achieved in the final third of the belt – the 'cooling strands' are used only as transport strands.

In 1999 DK built a second gas cleaning plant behind the existing electrostatic precipitator to keep the environmental limits for SO_2 as well as dioxins and furans within permitted limits. The plant consists of an injector for milk of lime, an injector for lignite coke and a bag filter for capturing solids.

Although the raw materials have not improved over the years, and if anything have deteriorated in quality, sinter productivity has improved considerably to reach 64t/h or a specific productivity of 24t/m²/24h (**Fig 4**).

Blast furnace

The DK blast furnace plant consists of two rather small blast furnaces of which normally the larger one, blast furnace #3 of 580m³ working volume and 5.5m hearth diameter is operating and the smaller BF#4 of 460m³ and 4.5m hearth is presently idle. Nominal output from BF #3 is 1000t/24h and that of BF#4 when working 500t/24h. Iron is tapped every 2 hours, desulphurised and cast on a casting machine to form pigs weighing 8 to 10kg.

The gas cleaning of the furnace exhaust consists of two steps: a dry precipitation of coarse dust in the dust catcher and a wet scrubber

	H_2O	Fe	Zn	C	S	CaO
BOF dust 1	9.2	62.1	0.6	1.2	0.2	6.5
BOF dust 2	0.0	43.3	11.6	0.8	0.05	14.2
BF Sludge	34.3	22.9	3.7	34.7	1.4	3.5
Mill Scale	6.5	68.0	0.05	0.8	0.03	2.1
Iron ore	7.5	66.3	0.01	0.04	0.01	0.02

Table 1 Typical raw material compositions for DK Process (%)

Element	Wt %
Zn	65-68
Pb	1-2
C	<2.0
Fe	<1.5
F	<1.0
Cl	<1.0
Na	<0.01
K	<0.15

Table 2 Analysis of DK Zinc concentrate from BF

Based on a presentations to 'Waste Recovery in Ironmaking and Steelmaking Processes' IoM3, London 13-14 Dec 2010

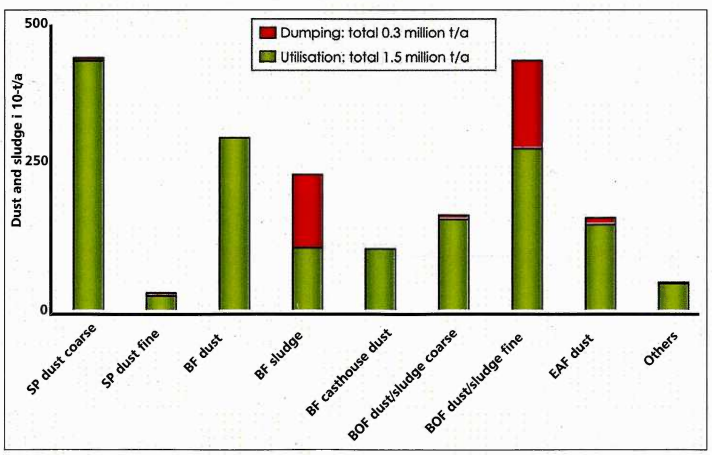

Fig 1 72% of iron and steelmaking dusts and sludges were recycled in Germany in 2006

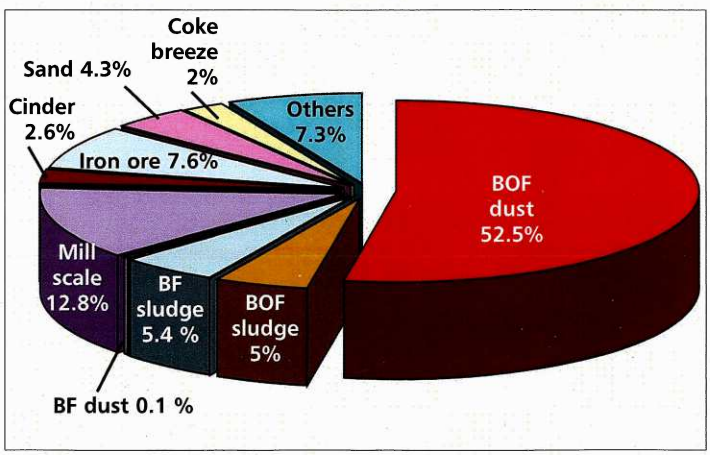

Fig 2 Raw material mix for DK sinter production

*Managing Director; DK Recycling und Roheisen GmbH; **Deputy Managing Director; DK Recycling und Roheisen GmbH, Werthauser Straße 182; D-47053 Duisburg, Germany e-mail hillmann@dk-duisburg.de

Quality	Si	Mn	P	S	C	Fe
DK MO	1.0-1.5	0.7-1.0	0.0-0.12	0.0-0.05	3.5-4.0	Rem
DK MIII	2.5-3.0	0.5-1.0	0.0-0.12	0.0-0.04	3.5-4.2	Rem
DK DKC	2.0-2.5	0.5-0.9	0.0-0.12	0.0-0.04	2.8-3.1	Rem
DK P-Eisen	2.0-2.5	0.5-0.8	1.2-1.7	0.0-0.04	3.5-3.8	Rem
DK Speigeleisen	1.0-2.0	14.0-15.0	0.0-0.15	0.0-0.04	4.0-5.0	Rem

Table 3 Some pig iron qualities of DK (wt %)

		DK BF	Conventional
Share of sinter in the burden	%	100	40-60
Si-content pig iron	Wt %	2-2.5	< 0.5
Slag amount	kg/t HM	400-450	200-250
Zn burden	kg/t HM	38	< 0.1
Alkali burden	kg/t HM	8.5	2-3
%CO2/(%CO2+%CO)	-	~ 30	~ 50
Off-gas temperature	°C	~ 350	~ 120
Productivity	t/(m³/24h)	1.4	2.5-3.5
Specific consumption of reducing agents	kg/t HM	700-720	480-550

Table 4 Typical operating parameters of a conventional blast furnace with that of the DK blast furnace

	Unit	DK SP	Conventional
Strand area for sintering	%	75	100
Coke Breeze consumption	kg/t Sinter	20	40
Productivity	t/m²/24h	24	40

Table 5 Comparison of DK Sinter plant versus conventional sinter plant

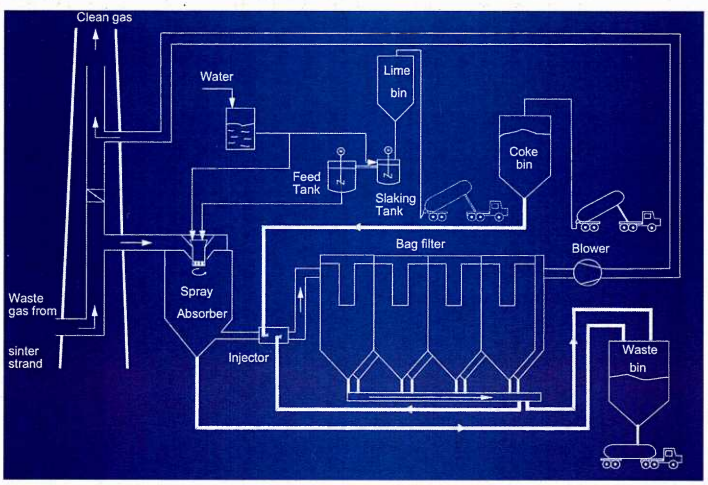

Fig 3 Flow through sinter preparation

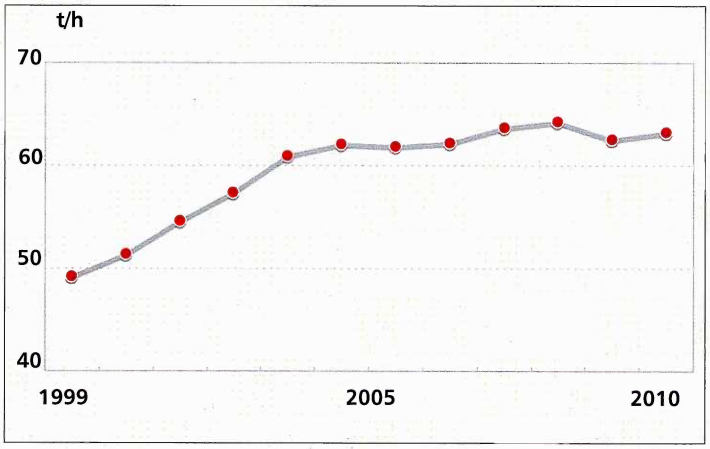

Fig 4 Improvement in sinter productivity

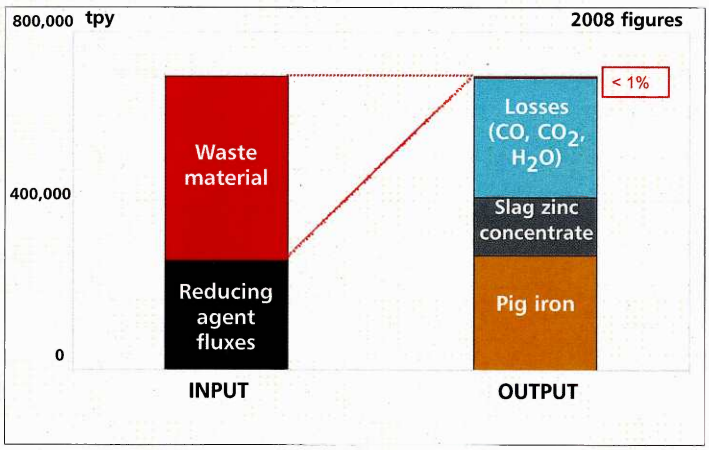

Fig 5 Material balance of the DK process

where the capture of fine dust which carries the zinc oxide takes place. The sludge from the wet gas cleaning is collected in a thickener and forms the second product of DK, the zinc concentrate.

Great improvements in blast furnace productivity have been achieved in the past 10 years with output now at 35t/h from about 25t/h in 2000. The improvement until mid 2005 was achieved by the introduction of process optimisation and further increased from mid 2006 with the introduction of oxygen enrichment to the air blast which ranges from 60Nm³ to 120Nm³ per tonne hot metal. Oil injection is employed at a rate of around 50kg/tHM to reduce the coke rate to 670kg/tHM.

Due to the extremely high zinc load in the furnace of 38kg/tHM, the sludge from the furnace arrives as a zinc concentrate with 65 to 68% of zinc content and very few impurities (**Table 2**). Compared to other secondary zinc raw materials the low content of fluorides and chlorides are an advantage.

In 2007, the amount of zinc concentrate processed peaked at 17-18kt (wet weight) which was sold to a smelter where it resulted in 9750t of zinc metal, but this fell by nearly 50% in 2009 during the recession when 5000t of metal resulted.

Besides the capability to recycle a variety of steelmaking residues, DK produces high quality foundry pig iron. **Table 3** shows typical analyses of some of the iron grades produced which number 80 different grades produced.

Recycling efficiency

The success of a recycling process can be measured by the amount of material which at the end of the process has to be treated as waste. The balance of DK in 2008 shows that less than 1% of the 430kt of processed waste material had to be dumped (**Fig 5**).

Table 4 shows a comparison of typical parameters of an integrated steelmakers blast furnace with that of the DK blast furnace.

Table 5 compares the sintering process for DK and conventional sinter production.

In summary, the following factors influence the feasibility of recycling dusts and sludges within an integrated works making it more economic to send these materials to a specialist recycler.

- Extremely small particle sizes leads to loss in productivity, especially during sintering;
- Residues can lead to higher emissions in the sinter plant, ie VOC, PCDD/F, heavy metals etc.
- Zinc in the blast furnace leads to higher coke consumption, refractory loss, formation of accretions etc.
- Alkalis have a great impact on coke behaviour in the blast furnace, leading to swelling of pellets etc.
- Although the content of valuables in the residues appears to be high enough for recycling, there are quantities of very harmful elements present for stable and cost effective production. ■

Contact
DK Recycling und Roheisen GmbH, Werthauser Straße 182;
D-47053 Duisburg, Germany
e-mail hillmann@dk-duisburg.de web www.dk-duisburg.de/