Reduction of Steelmaking Slags for Recovery of Valuable Metals and Oxide Materials

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Abstract

Extensive researches on slag reduction for recovery of valuable metals and oxide materials from metallurgical slags and other wastes using a DC-furnace with hollow electrode have been conducted in two major EU-projects with close cooperation between MEFOS, FEhS and CRM.

Steels slags and other residues were introduced into the reactor throughout the hollow electrode to the hot plasma. The materials were melted, reduced and mixed. The final products were a metal product, a slag product with targeted chemical composition and a dust fraction with high content of ZnO.

Different steelmaking slags and residues including BOF-slag with low and high V-content as well as EAF- and AOD-slags from stainless steel production, EAF dust, oily mill scale, hydroxide sludge, BOF and BF-dust have been treated. The slag products included a metallurgical powder for desulfurization of steel, hydraulic binder and slag stones for construction applications. The obtained metals are rich in Fe, Mn, V and Cr depending on the treated slag and residues. The environmental compatibility and mechanic properties of the slags have been improved after slag reduction.

1 Introduction

Steel industry produces annually huge amounts of wastes/ by-products as shown in Table 1. In addition to those listed in Table 1 there are large amounts of blast furnace sludge, millscale oily millscale, hydroxide sludge etc. generated annually. Most of them are currently disposed. The solid wastes generated from steel industry consists mainly of
a) stable oxides such as CaO, SiO_2, AlO_3
b) less stable oxide such as FeO, Cr-, Ni-, Mn- and P-oxides
c) volatile inorganics such as Zn, Pb, Cd, etc.

The current situation of solid wastes within the steel industry is described shortly in the following.

<u>Steel slags</u>

On an average, more than 70% of slags of carbon steel making are utilized in areas such as road building, cement industry, water constructions within EU and the other industrialised countries. There is however still million tons of disposed steel slags in EU. There is almost no utilization of slags from stainless steel making due to their high content of chromium and poor physical properties.

The potential problems associated with utilization of steelmaking slags are:
- volume-stability of the slags.
- potential leaching of heavy metals such as Cr, V, etc.

<u>EAF dust</u>

EAF dust from both carbon steel and stainless steel making has been classified as hazardous waste in most of the developed countries. Today the steel plants have to pay 100-400 US$/ton for external treatment. Within EU there is still short of capacity of dust treatment. In addition to that there is huge amounts of stored EAF dust waiting for a cheaper treatment technology.

<u>Millscale</u>

Millscale is usually recycled back to the primary furnaces such as sinter plants, blast furnaces or EAFs. There are also external markets for this product.

<u>Oily millscale and hydroxide sludge</u>

These are two difficult materials with no commonly accepted treatment technology. Disposal cost of these materials is higher than that for EAF dust.

That is, in order to stabilize and improve the existing market of the steel slags, to solve the problems associated with the fine-grained wastes and in order to meet the ever increasing environmental demands such as leaching limits of heavy metals, it is of great importance to investigate the possibilities of treatment of slag and all the other in-plant by products for metal recovery and slag stabilization in one and the same reactor. This will release the recycling burden of all the metallurgical furnaces such as the blast furnace, the EAF-furnace, the BOF-converter etc., so they could concentrate on steel production and leave the optimization of up grading of by-products to a separate plant having this as its core business.

This paper will summarize the activities and the main results from two major slag reduction projects. One for treatment of BOF-slag and the other for treatment of steelmaking slags from stainless steelplants. Other solid wastes were also treated. These projects were partially financed by EU (ECSC and Brite Euram-programs), and were carried out by close colaboration between MEFOS, CRM and FEhS.

2 The IPBM concept

The process concept IPBM, stands for <u>I</u>n <u>P</u>lant <u>B</u>y-product <u>M</u>elting process.

The demands on the IPBM process for slag reduction includes:
- Efficient reduction of steel slags and other solid wastes.
- The possibility to treat large amounts of slag in a continous or semi-continous mode.
- The possibility to add virtually all internal wastes/ by-products, such as BF- BOF- and EAF-dust, millscale, noxious spent refractories etc., during the reduction.

The chosen reactor for the test campaigns at MEFOS was a DC furnace with a hollow electrode for simultaneous treatment of slags and fine-grained products including those with volatile metals such as zinc and lead.

The IPBM concept is illustrated in Figure 1.

Steel slags and other fine-grained by-products, such as dust, millscale etc, are charged through the hollow electrode. By charging through the electrode all materials are going through the DC-plasma region and are efficiently treated. The material requires very little pre-treatment and both dusts and granular materials can be charged.

3 Materials

The treated materials are listed in Table 2. Besides the steel slags, fine-grained wastes such as EAF-dust, millscale, oily millscale, BOF dust, BF dust, hydroxide sludge and scrap residue was also treated. Mixture SS is a mixture consisting of stochiometrical amount of the generated EAF dust, oily millscale, hydroxide sludge and normal millscale from a stainless steelplant.

The used reductants being tested included coke breeze, anthracite and petroleum-coke. Other materials used are slag formers such as sand and lean bauxite for slag modification.

4 Experimental procedure

Four test campaigns have been carried out at MEFOS, using the 3 MW DC-furnace as the basic equipment.

Process data such as power input, gas analysis, C-balance, feeding rate, specific energy consumptions (kwh/ton) etc was recorded second by second. Samples of slag , metal dust and temperature were performed accordingly without unnecessary operation stop.

The slag products were air cooled, water cooled or granulated by jet quenching using a special equipment developed by FEhS, shown in Figure 2.

5 Results and technical evalution

Pre-investigations for the pilot test campaigns
In order to perform the large-scale pilot plant test as efficient as possible extensive pre-investigations were carried out prior to each campaign by CRM, FEhS and CSM, such as viscosity measurement, melting point determination and small scale reduction test.

Results from the slag reduction tests in the 3 MW DC-furnace with hollow electrode
Four test campaigns were performed in the MEFOS 3 MW DC-furnace. The two first ones with vanadium rich BOF slag and the third with normal BOF slag.

In the 1st campaign various process parameters were studied, such as feeding rates, feeding materials and granulation technology. It was found that coke breeze was not sufficiently efficient for reduction of vanadium oxide.

The main objective of the 2nd campaign was therefore to find a more an efficient reductant aiming at a high V yield, over >80% and a high productivity in the furnace (ton slag/h).

It was also the objective to prepare sufficient amounts of water-cooled treated slag (hydraulic binder) by addition of bauxite, sand and/or scrap residue for further evaluation by CRM.

High V-containing BOF-slag of 0-6 mm was used as the base material in this campaign. Coke, anthracite and pet-coke were tested for comparison of the effect on the V_2O_5-reduction and in Table 3 relevant process data and all final slag analyses from this part of the pilot campaign are presented.

Sand was the only slag former used and the sand to BOF-slag ratio was 0.48 in all tests. The reductant to BOF-slag ratio was 0.13.

Coke, anthracite and pet-coke were used for slag reduction in various charges. It was clearly demonstrated that anthracite and pet-coke are much better reductants for V_2O_5-reduction than coke. In the rest of the 2nd campaign anthracite was chosen as the main reductant for most of the tests since it showed good reduction properties and is cheaper than pet-coke.

With anthracite as reductant, a V-recovery of 80% was obtained with a feeding rate of 1.0-1.75 ton BOF-slag/h using the MEFOS DC-furnace and slag temperatures of 1550-1650°C. With coke a V-recovery of <80% during reduction was obtained with a feeding rate of 0.5-1 ton BOF-slag/h campaign, although at very high temperatures (1700-1800°C).

Reduction of coarse BOF-slag (8-30 mm) was also tested. The problem observed in the beginning was that most of the input BOF-slag remained unreacted, floating on the slag surface and tended to gather towards the furnace wall and the tapping hole. The conclusion is that the DC-furnace with its present equipment is not suitable for melting coarse material.

The main objective of the 3rd campaign was to produce and provide for various slag products, such as clinker material, metallurgical powder and hydraulic binder using low vanadium BOF-slag as the base material.

Some results from the 3rd campaign are shown in Table 4. The feeding rate was controlled at 1000kg slag per hour and the charging time was normally two hours.

Reduction of FeO and P_2O_5 by anthracite in the DC-furnace seems easy. In most cases of total reduction, the FeO-content has been reduced to below 1% and the P_2O_5-content below 0.2%. The reduction of MnO was more difficult as observed also during campaign 2.

The expected chemical composition of the various products is very close to the target composition. The product from charge 1 was supposed to be a product as raw material for cement clinker. The product from charges 2 and 3 looked like normal slag stone after tapping. During cooling, this product disintegrated completely into powder, a so-called metallurgical powder, due to the $\beta \rightarrow \gamma$-C_2S transformation. The products from charge 4 and 5 have been granulated in a special granulation apparatus and also by tapping slag directly in a water-containing tank.

Special test (No 6-9) included a dephosphorisation trial, treatment of scrap residue and reduction of various fine grained material including a mixture of mill scale, BOF and BF dust, and EAF dust from both stainless and C-steel making. During the second campaign, difficulties in heating scrap residues, such as slag foaming and boiling were observed. For charge 4 and 5 scrap residues were used during this campaign. Not a single problem occurred or was observed. The process thus seems technically to be an excellent tool for destruction of this hazardous waste.

No specific problems were observed for treatment of the mixture of millscale, BOF- and BF-dust (test no 8). Over 95% of the iron was recovered. The Zn-content in the slag was less than 0.02%, which means a 99% Zn-removal.

In the 4th campaign EAF-slag, AOD-slag, EAF-dust, oily millscale and hydroxide sludge from stainless steel production were treated. A metal containing typically 15-20% Cr and 4-5% Ni was obtained. The slag was also granulated by jet quenching device as described previously and shown in Figure 2.

The chemical analysis and leaching results of the slags before and after DC-furnace reduction is shown in Table 5.

As shown in the table, the Cr-content could be reduced to as low as 0.02%. On the average, the Cr-recovery was over 90% and Ni-recovery close to 100%.

The leaching of chromium of the reduced slag was 10-100 times lower than that of the untreated reference slag.

Leaching tests and volume stability tests of the slag products obtained from one of the IPBM campaigns have been extensively described in another paper at this conference[2)]. Volume expansion of the slag was much lower than the demands for aggregate for road constructions. The leaching properties of the slag before and after reduction was compared and shown in Table 5.

6 Evaluation of the obtained slag product

Clinker material

A mineral mixture consisting of 70.6% limestone, 19.4% clay rock and 10% IPBM slag (partially reduced) was prepared at FEhS as a cement clinker meal. The mechanic and physical properties of this slag-based clinker meal has been tested according to EN 196, and compared with an ordinary Portland cement (OPC) as shown in Table 6.

It was concluded that a clinker cement material could be prepared using the obtained IPBM-slag.

Hydraulic binder

Hydraulic binder has been produced by granulation in a water tank during tapping of slag with a basicity around 1.0 and by granulation with the FEhS jet quenching equipment. Due to the rapid quenching the obtained slag contained more than 95% glass. Figure 3 shows the XRD-diagram with the hump, typical of a glassy substance.

Figure 4 shows the obtained hydraulic binders prepared by quenching with the jet quenching device.

Metallurgical powder (MP-slag)

Metallurgical powder has been prepared from campaign 1 and 3. Table 7 shows the typical analyses of two samples from campaign 3.

Both MP-1 and MP-2 were transformed completely into a fine dust during cooling. The strong γC_2S-peaks shown in Figure 5 confirmed the $\beta \rightarrow \gamma C_2S$ transformation and explained well the autogeneous disintegration of the obtained MP-slag after cooling.

Figure 6 shows the obtained fine MP.

About 2 tons of MP were tested in a steel work in Luxembourg and compared with their normal operation of secondary metallurgy using synthetic calcium aluminate slag. The summary of the test is shown in Table 8.

It was found that the S-removal capacity of the prepared IPBM slag from campaign 3 was close to that of purchased aluminates.

Metals

The typical metals obtained from these campaigns are summarized in the following.

	Prepared from	%V	%Mn	%P	%Cr	%Ni
M1	BOF-slag, high V	10	4	~0,6		
M2	BOF-slag, normal		4	0.5-1.5		
M3	Stainless steel slags				15-20	4-5

For recovery of vanadium in M1, further processing of the metal is necessary for removal of both P and Mn.

For M2, it was demonstrated that it could be used as water pipe (as cast iron) or iron granules. For recirculation to BOF, P-removal has to be done first.

For M3, this metal can be returned to the AOD-converter directly.

7 Conclusion

It has been demonstrated in pilot plant scale (3MW and 1-2 ton/h) that the DC-furnace with hollow electrode is a flexible and efficient reactor for treatment of steel slags and most of the other solid wastes generated within a steel plant. Metals such as iron, vanadium, chromium and nickel were recovered in a metal (alloy) phase and the stable oxides were transferred into various slag products accordingly by modification and quenching. Clinker cement material, hydraulic binder and metallurgical powders of good quality have been successfully prepared.

8 References

[1] The management of Steel Plant Ferruginous By-products, IISI, Brussels, Committe on Environmental Affairs and Committe on Technology, 1994.

[2] Johan Eriksson, Guozhu Ye, Michael Kuhn and Peter Drissen, “Characterisation of slag products obtained through reduction of stainless steel slags”, to be presented in this conference.

9 Acknowledgement

This paper is based on results from two major EU-projects. One is “The In-plant By-product Melting (IPBM) Process” partially financed by ECSC and the other one “ETEUSCE-Economical Technical and Ecological Utilization of Treated Slag in civil Engineering of High Quality Demands” partially financed by Brite-Euram program. These financial supports are highly acknowledged.

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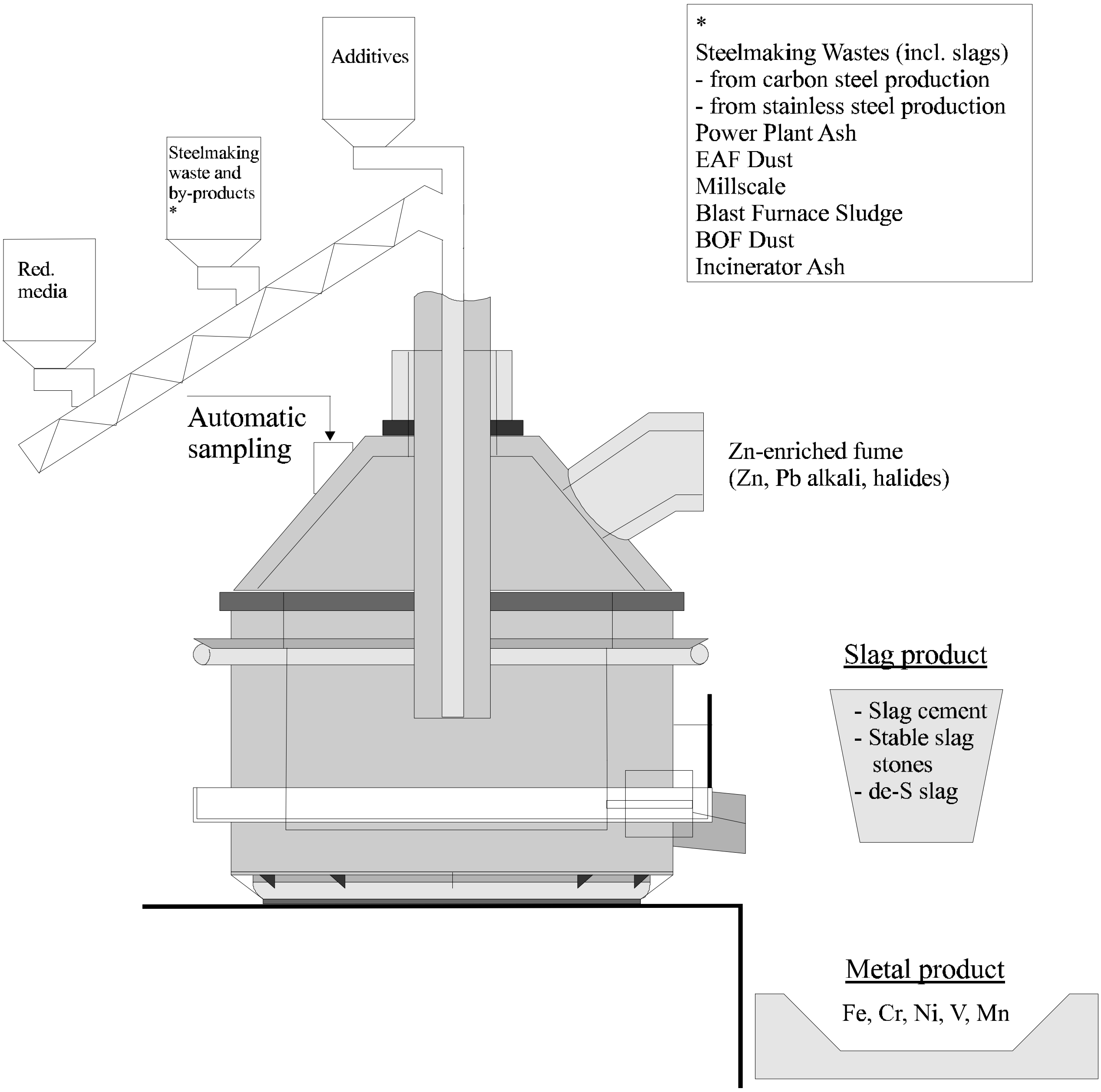

Figure 1: The IPBM concept

Figure 2: The FEhs granulation device

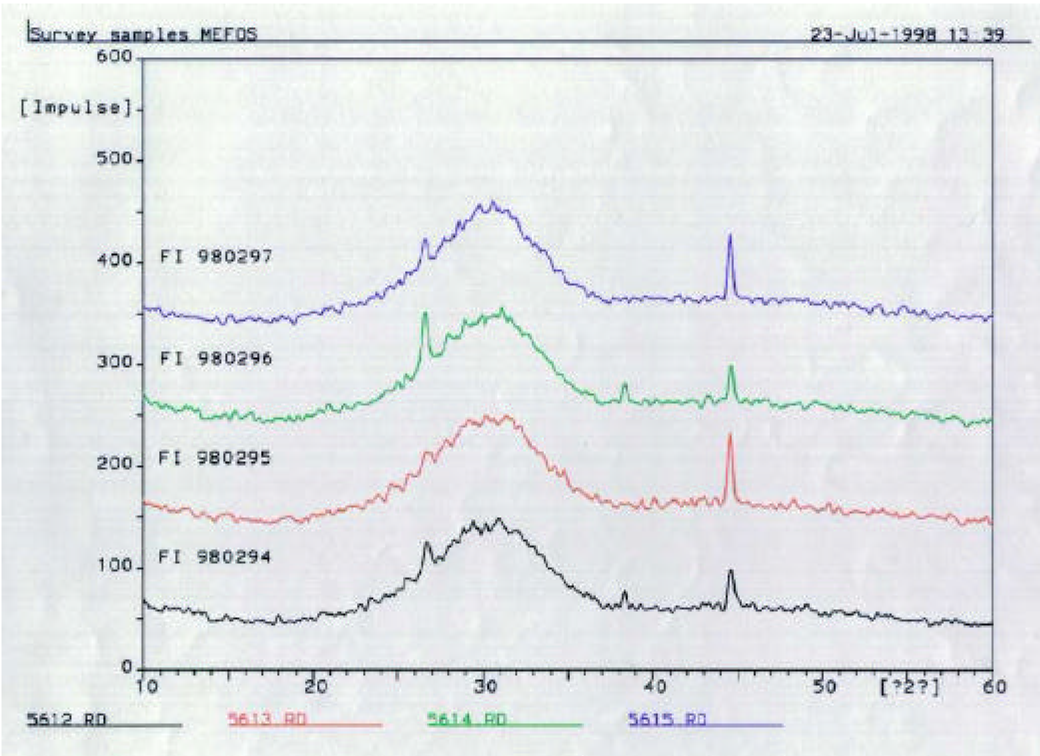

Figure 3: XRD-diagram with the hump typical of a glassy substance

a) Hydraulic binder No 1

b) Hydraulic binder No 2

Figure 4: Hydraulic binders produced during the IPBM campaign no 3

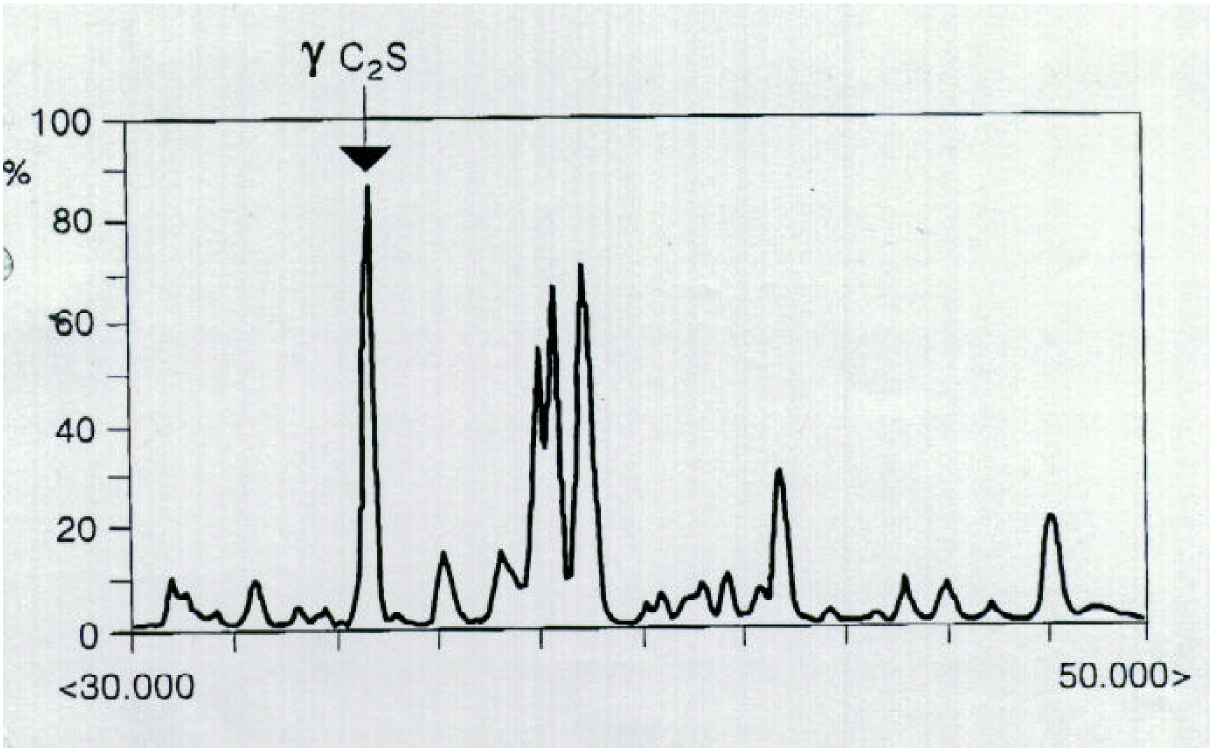

Figure 5: XRD-diagram of the metallurgical powder produced during campaign no 3

a) Metallurgical powder from charge No 2

b) Metallurgical powder from charge No 3

Figure 6: Metallurgical powders produced during the IPBM campaign no 3

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Table 1 Quantities of solid wastes generated annually in the steel industry

	World (Mtons)	Used or treated (%)	Sweden (Ktons)	Major concerns	Applications and practice today
BOF-slag	90	75	350	Free lime, heavy metals	Back to BF, roads, landfill, disposal
EAF-slag	25	77	200	Leaching of heavy metals	Weathering asphalt, disposal
BOF-dust	15	40	70	Too low Zn for recovery; too high Zn for recycling	Back to BOF or BF, disposal
EAF-dust	4	40	36	Hazardous wastes	Waelz kiln process, expensive; disposal

Table 2 Chemical analysis of the materials used in the pilot campaigns, %

	Stable oxides				Less stable oxides to be reduced								Volatile metals	
	CaO	SiO2	Al2O3	MgO	Fe	FeO	Fe2O3	MnO	Cr2O3	NiO	V2O5	P2O5	Zn	Pb
BOF-slag, V-rich	42.2	9.33	1.38	10.8		24.45		4.02	0.17		4.8	0.52		
BOF-slag, normal	51.04	11.28	1.6	1.2		23.07		3.67						
EAF-slag, SS*	38.8	30.4	5.15	8.47			2.57	3.95	6.74	0.16				
AOD-slag, SS	56	25.9	3.84	6.88			0.60	0.57	0.81	0.04				
EAF/AOD-mix slag	39.4	29.1	8.09	12.6			1.53	1.82	3.72	0.06				
Fayalite slag	2.5	35.7	4	1.2			51.6	0.5					1.5	
Sand	2.37	70	14	1.21			4	0.07				0.105		
Bauxite, lean quality	1.8	4.3	65				27.8							
Scrap residue**	11.07	23.78	5.6	1.64	5.93	13	17.5	1.21	0.81		0.1	0.93	1.73	0.49
EAF dust, C-steel	3	2	0.4	1.82			49.5	1.73					25.4	2.31
EAF dust, SS	20.4	2.88	0.16	0.57			40.6	5.82	15.7	4.6			2.49	
Secondary dust, SS	0.26	0.80		1.16			71.1	1.61	15.6	7.01				
Hydroxide sludge, SS	38.7	2.13	0.87	1			14.4	0.33	3.67	2.37				25%F
Oily millscale, SS	0.23	1.04	0.61				71.8	1.45	10.9	4.67				
Millscale, SS	0.4	1.4					75.3	2	14	5.7	0.1			
Mixture SS***	17.3	2.2	0.26	0.57			46.2	3.7	13.2	4.6			1.0	4%F
Mixture BBM****	19	7	1.6	3.9		2.7	55.2	0.7	0.08		0.14		0.9	

* SS= from stainless steel making

** Scrap residue is a solid waste generated during scrap transport and consists of metal wire, wood pieces, plastics, rust and sand

*** Mixture SS consist of 54%EAF dust, 16% hydroxide sludge, 14% millscale, 9% secondary dust and 7% oily millscale, all from stainless steel production

**** Mixture BBM consists of 40% BOF-dust, 40% oily millscale and 20%BF-dust, all from an integrated steel plant

Table 3 Relevant process data and final slag analyses, pilot campaign no 2

Test no	Feeding rate BOF-slag tonnes/h	Slag temp °C	MWh/ ton BOF-slag	Fe %	CaO %	SiO_2 %	MnO %	P_2O_5%	Al_2O_3 %	MgO %	V_2O_5 %	V-yield
	Reduction with coke 3-6 mm											
1	0.5	1620	1.3	5.21	28.2	18.3	n.a.	0.19	5.63	9.06	4.50	10
2	0.5	1650	2.0	1.86	33.4	27.5	n.a.	0.15	6.04	10.5	3.28	34
	Reduction with petro-coke 0-6 mm											
3	1.0	1630	2	0.58	36.8	34.0	3.65	0.002	6.65	14.4	0.60	88
	Reduction with anthracite 0-6 mm											
4	1.0	1617	1.7	0.44	38.3	29.4	9.50	0.05	5.67	12.0	1.57	67
5	1.0	1650	1.44	0.41	36.9	35.2	2.44	0	7.23	14.6	0.34	93
6	1.25	1640	1.46	0.65	38.0	35.6	4.12	0	6.89	12.0	0.96	81
7	1.5	1680	1.42	0.80	35.0	35.9	4.70	0.02	7.01	11.3	1.17	77
8	1.75	1585	1.43	0.46	35.4	37.0	3.80	0.01	7.12	11.2	1.01	80
9	1.75	1549	1.39	0.91	37.1	34.7	3.40	0.04	6.80	12.2	1.1	78
11	1.0	1553	1.41	0.61	32.9	33.8	3.02	0.01	12.44	12.3	0.98	80
-	BOF-slag analysis			18.4	41.2	9.36	4.34	0.55	1.43	11.3	4.94	

Table 4 Results from test 1-5, in campaign no 3

Test no	Product	Slag modi-fier	Slag temp °C	MWh/t on BOF-slag	Ratio Antr/ BOF-slag	Antr/ Feed		Fe	CaO	SiO_2	MnO	P_2O_5	Al_2O_3	MgO	Cr_2O_3
1	Clinker raw material	Sand Bauxite	1735	1.20	0.1	0.08	Target	3.7	62-66	20-21			4.7	<5	
							From test	4-3	54.7	20.8	3.5	2.2	6.9	2.2	0.24
2	Metallur-gical powder	Bauxite	1680	1.25	0.19	0.12	Target	<2	50-55	16			22	2-10	
							From test	0.35	56.6	19.6	1.18	0.2	21.9	2.85	0.03
3	Metallur-gical powder	Bauxite	1640	1.30	0.22	0.14	Target	<2	50-55				25-30	2-10	
							From test	0.3	54.2	13.6	1.75	0.47	27.3	1.81	0.03
4	Hydraulic binder	Scrap residue Bauxite	1665	1.20	0.72	0.13	Target	<2	45	33			14	2.5	
							From test	1.81	41.8	31.5	51.7	0.06	17.3	4.41	0.08
5	Hydraulic binder	Scrap residue Bauxite	1620	1.15	0.40	0.12	Target	<2	45	33			14	2.5	
							From test	0.45	44.5	34.4	0.93	0.04	14.0	4.41	0.04
-	BOF-slag analysis	-	-	-	-	-	-	18.4	51.0	11.3	3.67	2.56	1.60	1.20	-

Table 5 Reduction of stainless steel slags, analysis and leaching test before and after treatment

	EAF-slag	Reduced EAF-slag 1	Reduced EAF-slag 2	Reduced EAF-slag 3	Reduced EAF-slag 4	Reduced EAF-slag 5	Reduced EAF-slag 6	AOD-slag	Reduced AOD-slag	Mix-slag	Reduced Mix-slag 1	Reduced Mix-slag 2	Reduced Mix-slag 3
CaO	38.8	43.82	49.45	45.35	39.7	38.66	39.02	56	52.05	39.4	40.51	42.28	40.31
SiO2	30.4	35.35	34.27	36.21	24.39	33.75	35.87	25.9	33.23	29.1	32.99	31.06	31.23
Al2O3	5.15	4.86	7.65	5.06	31.01	13.73	8.38	3.84	6.39	8.09	9.07	12.07	7.23
MgO	8.47	9.98	5.5	7.23	4.75	7.01	8.64	6.88	4.72	12.6	10.8	10.73	15.56
Cr2O3	6.74	0.59	0.02	0.71	1.65	0.45	0.36	0.81	0.01	3.72	0.37	0.28	0.23
Fe,tot	1.8	0.43	0.23	0.5	1.08	0.51	0.68	0.42	0.09	1.07	0.52	0.39	0.87
Leaching													
pH	12.4	11	11.5	11.2	11.1	11.1	11.4	12.4	11.3	11.8	10.7	11.2	11.1
Conductivity mS/m	770	27	9.4	34	39	36	79	814	45	166	18	50	37
Leached Cr tot, mg/kg	1.1	0.1	0.1	0.2	<0.1	<0.1	0.1	0.9	<0.1	13.4	<0.1	<0.1	<0.1

Table 6 Data from clinker cement test

Physical & mech. datas	Dim.	Lab.-cement	OPC: CEM I 32,5R	
		Properties	Properties	Requirements
Interval		2d / 7d / 28	2d / 7d / 28d	2d / 28d
Compressive strength Ø	N/mm^2	20.4 / 36.0 / 52.1	23.1 / 39.6 / 49.3	≥10 / ≥32.5 <52.5
Ttensil strength Ø	N/mm^2	4.2 / 6.4 / 7.6	n.a. / n.a. /	-
Dyn. modulus of elasticity Ø	N/mm^2	27587 / 34764 / 38294	n.a. / n.a. / n.a.	-
Wwater demand	% by	28.0	26.5	-
Setting time	h:min	Start:3:55; End:4:25	Start:2:33; End:3:55	St.: ≥1:00; E.:≤12:00
Le-Chatelier-Test (C-A)	mm	4.0-3.0 = 1.0	0.5	≤10.0
Spreading	cm	15.7	n.a.	-
Specific surface	cm“/g	3520	3130	-
Insoluble residue	% by	0.03		≤5.0
Sulphate SO_3-content	% by	0.27		≤3.5

Table 7 Chemical composition of metallurgical powder

	Fe	CaO	SiO_2	MnO	P_2O_5	Al_2O_3	Cv_2O_3
MP-1	0.35	56.6	19.6	1.18	0.2	22	0.03
MP-2	0.3	54.2	13.6	1.75	0.47	27	0.03

Table 8 Comparison of desulfurization by MP-slag from IPBM-campaign with that of current practice

	Current practice	IPBM trials with powder no 2	IPBM trials with powder no 3
Quantity of slag used (kg)			
- lime	1000-1200 kg	650	600
- Al_2O_3	400-600 kg	750	800
Al_2O_3-content of the carrier (%)	38-40	20	26
Composition of the secondary metallurgy slag			
- CaO	48	42	47
- Al_2O_3	16-17	11.5	14
- SiO_2	22-23	23	26
- Total Fe	0.7-1	2	0.8
- MgO	9	18	8
- MnO	0.2-0.4	0.6	0.6
Final S-content in the steel (%)	0.026	0.029	0.035

Working conditions at the secondary metallurgy

1) Steel quality: 150 t
2) Treatment duration: ca 60 minutes
3) Purpose of the treatment
   a) temperature homogenisation and adjustment 1600°C
   b) de-S of the steel (S before: 0.06-0.09%, S after: <0.035%)
4) Steel composition (before contineous casting) 0.08%, 0.17%Si, 0.8-1.4% Mn, <0.035%S