ISSN 2176-3135

RECOVERY OF CHROMIUM AND NICKEL FROM WASTE MATERIALS USING THE OXYCUP PROCESS[1]

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Abstract

The OxyCup process shall be applied for the recovery of chromium and nickel from residues from the stainless steel production. Thermo-chemical model calculations in combination with recent experimental investigations demonstrate that high recovery rates for chromium and nickel can be expected. TISCO, the largest Chinese stainless steel producer therefore already ordered two OxyCup plants for both, residues from stainless steel production and residues from ordinary carbon steel production. Both lines will start operation in the beginning of 2011.

Key words: Oxycup; Recovery of chromium and nickel.

RECUPERAÇÃO DE CROMO E NÍQUEL DE RESIDUES COM O PROCESSO OXYCUP

Resumo

O processo OxyCup esta sendo aplicado na recuperação de cromo e níquel dos resíduos da produção de aços inoxidáveis. Cálculos e modelamentos termoquímicos em combinação com recentes pesquisas experimentais demonstraram que altas taxas de recuperação podem ser atingidas. TISCO, o maior produtor chinês de aços inoxidáveis encomendou para esta finalidade duas plantas OcyCup, tanto para residuos da produção de aços inoxidáveis como para residuos da produção de aço carbono. As duas plantas entrarão em peração no inicio do ano 201.

Palavras-chave: Oxycup; Recuperação de cromo e níquel.

[1] Technical contribution to the 40th International Meeting on Ironmaking and 11h International Symposium on Iron Ore, September 19 – 22, 2010, Belo Horizonte, MG, Brazil.
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ISSN 2176-3135

1 INTRODUCTION

The OxyCup technology for the recovery of liquid hot metal from wastes of integrated steel plants started operation in 2000 at ThyssenKrupp Steel, Duisburg, Germany and has produced successfully since that time. In this process dusts and sludge are agglomerated to self-reducing bricks with help of addition of carbon fines and cement. These bricks are charged together with more or less large pit scrap residues, lump coke and additives. In contrast to many other technologies which cannot charge large sized pit scraps and skulls and only deliver a solid iron product, OxyCup produces liquid iron as well as slag and gas. All these products are close to blast furnace qualities.

After the successful start-up of the process at TKS, also European stainless steel producers showed interest in this technology. In most cases they lack in own processes for the recovery of chromium and nickel from their residues and have to send their materials to external companies far away like ScanDust in Sweden. Therefore, Küttner has promoted the development of self-reducing bricks for chromium and nickel containing residues and conducted a number of tests which are described in the following. Reduction of the metal oxides is mainly done by carbon monoxide that is produced by carbon gasification inside the brick. The basic reactions are:

$CO_2 + C \rightarrow 2\ CO$ “Boudouard” reaction starts at temperatures > 900℃

$x\ CO + MeO_x \rightarrow Me + x\ CO_2$ Me = Fe, Cr, Ni Reduction reactions

2 RESIDUES FROM STAINLESS STEEL PRODUCTION

The stainless steel production route as a rule comprises many production and treatment steps like EAF, converter, AOD and VOD carbon removal. As usual, all these individual steps produce certain residues in form of dust, sludge, mill scale and lumpy pit scrap. **Table 1** shows typical analyses of a selection of these residues.

Table 1 - Analyses of residues from stainless steel production

Raw material		Total residue fines mix	Residues						
			EAF 1 dust	EAF 2 dust	AOD 1 dust	AOD 2 dust	Steel sludge	Steel coarse dust	BOF Chips
Amount wet	g/mix	106.168	20.000	7.200	20.000	1.455	39.837	8.586	9.091
Moisture	%	10,16	0,0	0,0	0,0	1,0	26,6	1,00	1,00
Amount dry	g/mix	95.380	20.000	7.200	20.000	1.440	29.240	8.500	9.000
Amount of water	g/mix	10.788	0	0	0	15	10.597	86	91
Analysis		%		%	%	%			
Fe, total calculated	%	42,20	36,74	25,97	31,86	35,44	49,37	38,09	71,95
Gangue, total	%	30,34	19,15	19,49	28,50	20,51	46,75	28,39	18,06
C	%	2,09	3,33	0,68	1,33	2,09	2,50	2,69	0,27
Fe,met	%	0,06	0,00	0,00	0,00	0,00	0,00	0,00	0,60
FeO	%	28,63	17,10	10,00	15,60	17,50	37,05	36,86	64,80
Fe2O3	%	28,42	33,50	26,00	28,20	31,20	29,40	13,50	30,00
CaO	%	12,43	10,25	7,22	17,18	9,50	12,08	9,74	15,00
SiO2	%	4,49	6,31	7,04	6,63	6,26	1,77	5,14	1,56
Al2O3	%	0,66	0,70	0,97	0,86	1,04	0,22	0,43	1,47
MgO	%	3,67	1,89	3,76	3,60	3,71	3,28	13,08	0,03
ZnO	%	1,23	1,89	10,13	0,25	0,62	0,01	0,01	0,00
SO3	%	0,13	0,20	0,20	0,17	0,29	0,07	0,06	0,11
P2O5	%	0,05	0,10	0,05	0,03		0,04	0,05	0,06
Cr	%	8,02	11,00	6,46	8,08	5,70	5,22	20,35	0,31
Ni	%	2,60	4,24	2,49	4,72	3,35	0,10	0,11	4,66
Balance	%	6,86	9,49	20,17	12,05	16,72	8,26	-2,02	-18,88
Total	%	*100*	100,00	0,68	100,00	100,00	100,00	100,00	100,00

ISSN 2176-3135

X-ray diffraction analysis allows a semi quantitative determination of the crystal phases of the residues. **Figure 1** shows a typical diffraction spectrum of a chromium and nickel containing dust. Beside some nickel present as metal all chromium is present as chromite (FeCr2O4). Chromite was proved to be the main chromium compound in most of the residues except in grindings, where high amounts of metallic chromium are present.

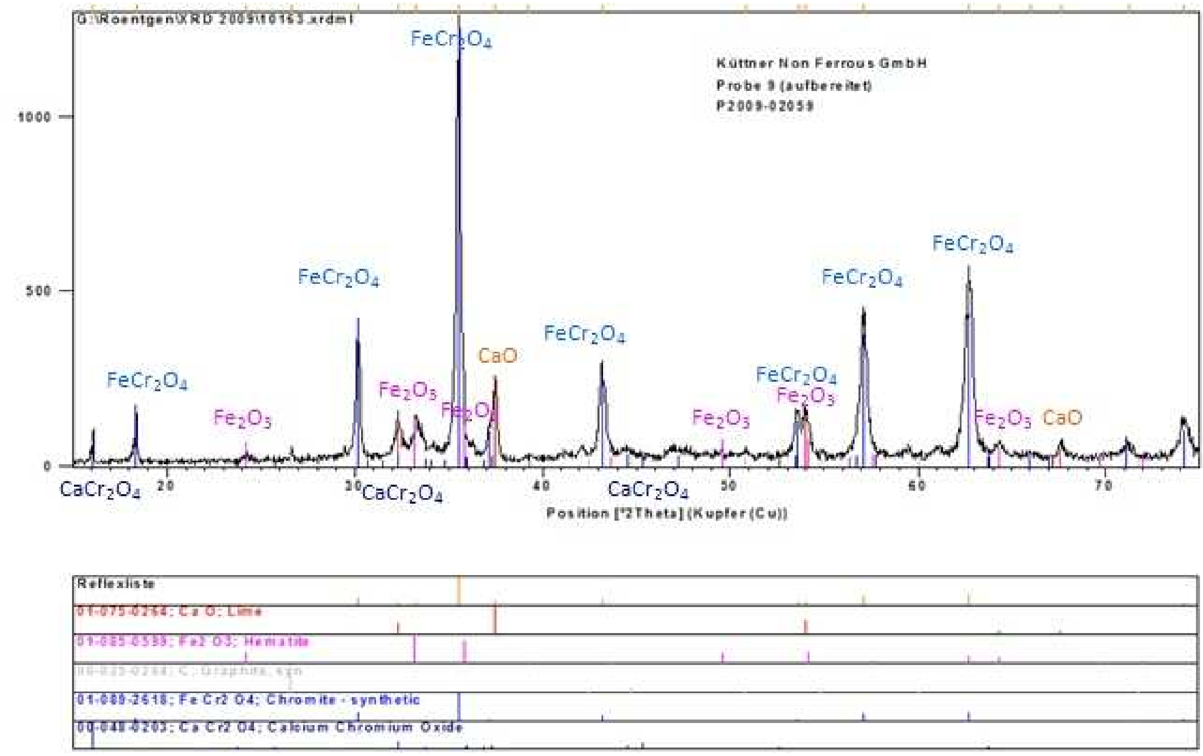


Figure 1 - X-ray diffraction picture of a typical residue from stainless steel production.

The following **Table 2** summarizes the results of 14 dust and sludge samples of different production sites indicating the main constituents with X, the side constituents with (X) and the trace compounds with Sp. Table 2 shows that beside chromium also iron is predominantly bound in chromite. As anticipated many samples also contain high amounts of free lime.

Table 2 - Semi quantitative phase analysis of 14 dust and sludge residue samples from stainless steel production.

	Sample No.	9	11	12	14	15	17	26	27	30	36	14	15	26	30
Mineral:	Formula:														
Quartz	SiO_2							SP		SP					
Graphite	C	SP	SP		SP	SP		SP	SP	SP		SP	SP		
Chromite	$FeCr_2O_4$	X	X	X	X	(X)	SP	X	X	X	X	(X)	(X)	(X)	X
Calcium-Chromite	$CaCr_2O_4$	SP		SP				SP							
Hämatite	Fe_2O_3	(X)	(X)	(X)	X	(X)					X	(X)	(X)		
met. Nickel	Ni				SP	SP		SP	SP	SP		SP	(X)	SP	SP
Fluorite	CaF_2				SP	SP		SP	SP	SP		SP	SP	SP	SP
Monticellite	$CaMgSiO_4$							(X)		(X)					
Periklas	MgO					(X)	(X)	(X)		(X)				(X)	(X)
Calcite	$CaCO_3$			(X)		SP	SP	SP	(X)				SP	SP	
Portlandite	$Ca(OH)_2$						SP						SP	SP	SP
Free lime	CaO	(X)		(X)	X	X	X	(X)	SP	(X)	SP	X	X	X	X

X := main component, (X) secondary component, SP := traces

ISSN 2176-3135

2.1 Self-reducing Bricks from Residues

For further investigations mixtures of the different residues were prepared in such a way that the percentage of the individual residues in the mixture resembles the yearly production. From these mixture test bricks were formed after admission of carbon fines for the internal reduction of chromite and FeOx and about 12% of cheap (blast furnace) cement. **Table 3** shows the composition of the final brick.

Table 3 - Composition of self reducing brick from stainless steel residues

Raw material		Total residue fines mix	Additives for C-Bricks			C-Bricks		Iron alloy	slag
			Coke fines	Cement binder	Water addition	g/mix	%	from brick	from brick
			Stoich.	Add.	Add.				
Amount wet	g/mix	106.168	16.029	14.442	10.232	145.615	116,00		
Moisture	%	10,16	2,0	0,0		16,00	16,00		
Amount dry	g/mix	95.380	15.708	14.442	10.232	125.530	100,00	6,03	4,20
Amount of water	g/mix	10.788	321			20.085			
Analysis		%	%	%	%	t/a	%	%	%
Fe, total calculated	%	42,20	0,21	1,89		40.554	32,31	81,01	
Gangue, total	%	30,34					27,20		
C	%	2,09	90,00	0,00		16.133	12,85	3,00	
Fe,met	%	0,06	0,00	0,00		54	0,04		
FeO	%	28,63	0,00	0,00		27.311	21,76		0,99
Fe2O3	%	28,42	0,30	2,70		27.542	21,94		0,00
CaO	%	12,43	0,00	63,30		20.994	16,72		60,00
SiO2	%	4,49	3,10	20,70		7.756	6,18		22,17
Al2O3	%	0,66	1,30	5,30		1.600	1,27		4,57
MgO	%	3,67	0,00	1,50		3.712	2,96		10,61
ZnO	%	1,23	0,00	0,00		1.170	0,93		
SO3	%	0,13	0,97	3,50		786	0,63		0,02
P2O5	%	0,05				52		0,09	0,00
Cr	%	8,02		0,00		7.647	6,09	10,76	0,00
Ni	%	2,60				2.478	1,97	4,73	0,00
Balance	%	6,86	4,33	2,10	100,00		6,04		
Total	%	*100*	100,00	100,00	100,00		100,00		

The amount of carbon fines (coke breeze, anthracite, char coal or other) in the brick is calculated according to the stoichiometric demand for reduction. Because of the high CaO/SiO2ratio in the brick gravel has to be charged to the furnace to adjust the basicity of the slag close to one.

Thermo-chemical investigations

By thermodynamic process simulation the reduction behavior of self-reducing bricks was studied. The calculations were carried out with help of "Equitherm" a computer program that allows the calculation of multi-phase systems comprising hundreds of components. This kind of equilibrium calculations give a good forecast about the distribution of chromium and nickel in iron and slag phase as a function of temperature, gas and brick composition. **Table 4** shows some of the calculated data.

ISSN 2176-3135

Table 4 - Input and output data of the thermo-chemical calculations for 1000kg bricks and 200kg coke

	Formula	Mol <in>	Mol <out>	kg <in>	kg <out>	% <in>	% <out>	Mol fraction
Gravel	SiO2	166.43	0.00	10.00	0.00	100.0	0.0	1.090E-05
Coke	C <F> ...	14986.26	0.00	180.00	0.00	90.0	0.0	-
	H <F> ...	1984.25	0.00	2.00	0.00	1.0	0.0	-
	N <F> ...	28.56	0.00	0.40	0.00	0.2	0.0	-
	O <F> ...	12.50	0.00	0.20	0.00	0.1	0.0	-
	S <F> ...	43.66	0.00	1.40	0.00	0.7	0.0	-
	Al2O3 ...	19.62	0.00	2.00	0.00	1.0	0.0	-
	CaO	17.83	0.00	1.00	0.00	0.5	0.0	-
	Fe2O3 ...	12.52	0.00	2.00	0.00	1.0	0.0	-
	MgO	24.81	0.00	1.00	0.00	0.5	0.0	-
	SiO2	166.43	0.00	10.00	0.00	5.0	0.0	-
Brick	Al2O3 ...	19.62	0.00	2.00	0.00	0.2	0.0	-
	C	14986.27	0.00	180.00	0.00	18.0	0.0	-
	CaO	1943.74	0.00	109.00	0.00	10.9	0.0	-
	Cr2O3 ...	1059.28	0.00	161.00	0.00	16.1	0.0	-
	Fe3O4 ...	1701.66	0.00	394.00	0.00	39.4	0.0	-
	MgO	570.66	0.00	23.00	0.00	2.3	0.0	-
	MnO	902.20	0.00	64.00	0.00	6.4	0.0	-
	MoO3	6.95	0.00	1.00	0.00	0.1	0.0	-
	NiO	535.55	0.00	40.00	0.00	4.0	0.0	-
	SiO2	432.73	0.00	26.00	0.00	2.6	0.0	-
Slag	Al2O3 ...	0.00	14.74	0.00	1.50	0.0	0.6	5.683E-03
	CaO	0.00	410.93	0.00	23.04	0.0	9.1	0.158
	CaAl2Si2O	0.00	0.00	0.00	0.00	0.0	0.0	1.348E-07
	CaMgSi2O6	0.00	0.04	0.00	0.01	0.0	0.0	1.389E-05
	Ca2SiO4 .	0.00	761.66	0.00	131.19	0.0	51.9	0.294
	CaS	0.00	27.28	0.00	1.97	0.0	0.8	0.011
	CaSO4 ...	0.00	0.00	0.00	0.00	0.0	0.0	3.809E-18
	CrO3	0.00	0.00	0.00	0.00	0.0	0.0	9.327E-15
	Cr2O3 ...	0.00	147.69	0.00	22.45	0.0	8.9	0.057
	FeO	0.00	20.76	0.00	1.49	0.0	0.6	8.004E-03
	FeS	0.00	0.17	0.00	0.02	0.0	0.0	6.726E-05
	MgO	0.00	562.70	0.00	22.68	0.0	9.0	0.217
	MgAl2O4 .	0.00	24.49	0.00	3.48	0.0	1.4	9.443E-03
	MgSiO3 ..	0.00	0.35	0.00	0.03	0.0	0.0	1.332E-04
	Mg2SiO4 .	0.00	3.27	0.00	0.46	0.0	0.2	1.261E-03
	MgSO4 ...	0.00	0.00	0.00	0.00	0.0	0.0	6.192E-22
	MnO	0.00	603.45	0.00	42.81	0.0	17.0	0.233
	Mn2SiO4 .	0.00	0.22	0.00	0.04	0.0	0.0	8.312E-05
	MnS	0.00	15.73	0.00	1.37	0.0	0.5	6.066E-03
	MoO3	0.00	0.00	0.00	0.00	0.0	0.0	8.907E-13
	Mo2S3 ...	0.00	0.00	0.00	0.00	0.0	0.0	1.651E-18
	NiO	0.00	0.01	0.00	0.00	0.0	0.0	2.052E-06
	NiS	0.00	0.00	0.00	0.00	0.0	0.0	8.835E-07
	NiS2	0.00	0.00	0.00	0.00	0.0	0.0	4.348E-14
	Ni3S2 ...	0.00	0.00	0.00	0.00	0.0	0.0	1.085E-11
	SiO2	0.00	0.03	0.00	0.00	0.0	0.0	9.983E-06
Iron	Al	0.00	0.00	0.00	0.00	0.0	0.0	1.067E-08
	Cr	0.00	1823.17	0.00	94.80	0.0	21.9	0.263
	Fe	0.00	3833.98	0.00	214.12	0.0	49.5	0.554
	Fe3C	0.00	406.36	0.00	72.96	0.0	16.9	0.059
	FeO	0.00	55.41	0.00	3.98	0.0	0.9	8.004E-03
	FeS	0.00	0.47	0.00	0.04	0.0	0.0	6.726E-05
	Mn	0.00	261.41	0.00	14.36	0.0	3.3	0.038
	Mo	0.00	6.95	0.00	0.67	0.0	0.2	1.003E-03
	Ni	0.00	535.54	0.00	31.43	0.0	7.3	0.077
	S	0.00	0.00	0.00	0.00	0.0	0.0	7.039E-08

The model calculations show that under the defined temperatures and gas composition the degree of reduction of chromite to metallic chromium and iron is dependent on the temperature in the self-reducing brick. Sufficient reduction of chromium is achieved above 1500℃. Iron and nickel do not require that high temperatures for complete reduction which can be anticipated from their lower heats of reduction.

ISSN 2176-3135

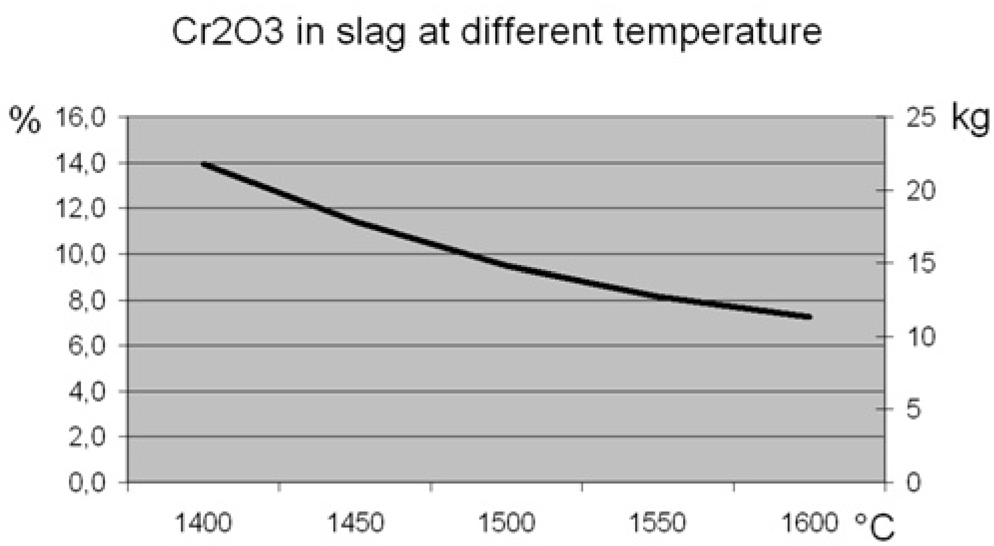


Figure 2 - Cr2O3 content in slag.

Because chromium oxide impairs the viscosity of the slag an estimation of the Cr2O3 concentration in the slag was made. Because of the relative overall high slag amountswhich are comparable to the amount of liquid alloy, the Cr2O3 concentration in slag will be kept even lower than shown in **Figure 2**.

Brick tests in solid state

According to the regular test procedures being applied for self-reducing bricks from carbon steel residues also the Cr and Ni containing bricks were tested. After agglomeration in a vibrating press (as used for regular concrete pavement bricks) the test bricks stayed as usual in humid atmosphere for 3 days cement hardening. **Figure 3** shows such a brick of approximately 65 mm height.

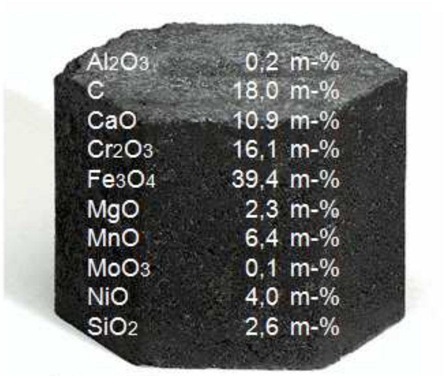


Figure 3 - Self-reducing test brick.

The main prerequisite for the brick use in the OxyCup shaft furnace is the physical stability of the bricks during their residence time in the furnace until melting. Two test methods are applied to measure the cold and hot compression strength. Cold compression strength is measured by pressing the brick under ambient temperature until breaking occurs. Cold compression strength between 8 Newton/mm2 and 12 Newton/mm2 were measured which by far exceed the minimal required strength of 5 Newton/mm2.

Measurement of the hot compression strength is combined with watching the reduction progress by continuous weighing of the sample brick. This procedure is well known for blast furnace people as RuL (Reduction under Load) test. Figure 4 shows a sketch of the equipment. Figure 5 shows the measured curves for temperature, weight loss and compression over time as well as a brick before and after RuL test.

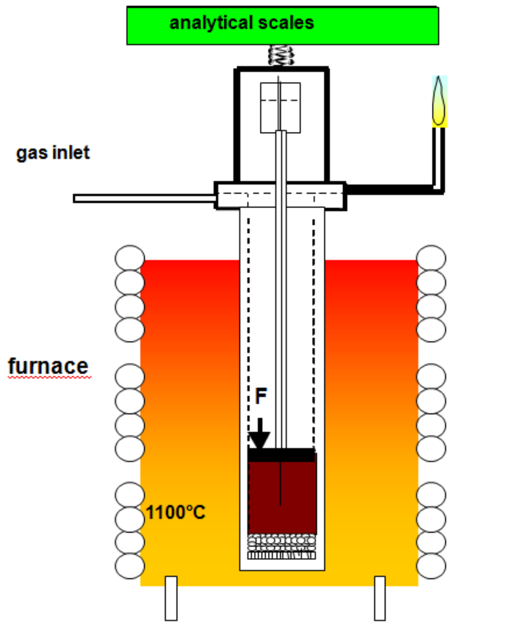
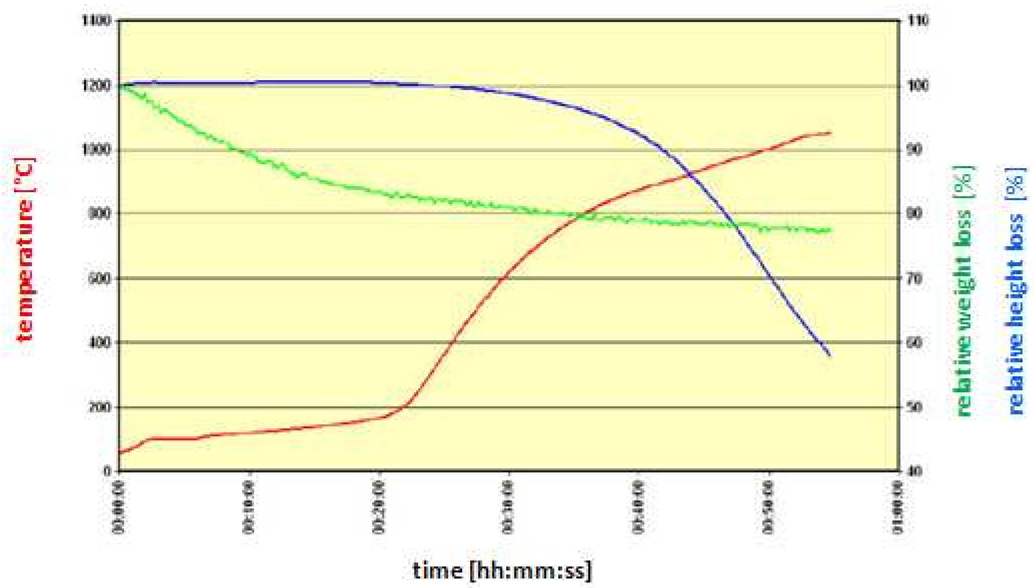


Figure 4 – RuL test equipment.



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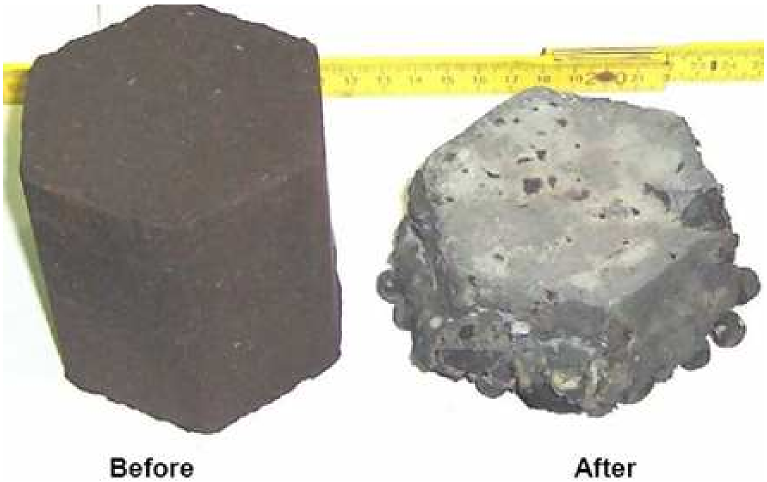

Figure 5 - Typical results of RuL test.

Above approx. 600℃ the height of the brick decreas es due to the load on top. The overall weight loss is 23% after 55 minutes. The temperature in the centre of the brick had then reached 1050℃. Chemical analysis af ter test showed 91% metallization of the iron. Unfortunately, the TKS lab had neither suitable equipment nor experience to analyze for metallic chromium (if any) after RuL treatment. However, RuL test equipment allows temperatures up to 1100° only. This is sufficient for testing the rate of iron ore reduction or normal iron oxide containing bricks. For the judgment of reduction of chromite containing bricks higher temperatures are necessary if the distribution of chromium and nickel into liquid alloy and slag is to be studied. Anyway, the test bricks passed the RuL test successfully with respect to hot strength and compressibility.

Smelt tests

To simulate the brick smelting i.e. reduction of the oxides of iron, nickel, chromium and subsequent melting to liquid iron alloy and slag temperatures up to 1500℃ are required. These trials were conducted in collaboration with the Technical University of Aachen (Prof. Pfeifer IOB).
A gas fired short shaft furnace was built that could carry a small crucible with the brick sample. A gas burner tangentially mounted fired around the crucible. Thermocouples were mounted to measure both the temperatures within the furnace and inside the brick sample through a bore hole. Figure 6 shows a picture of this equipment.

ISSN 2176-3135

Figure 6 - Gas fired test furnace for smelt-reduction trials.

The results of the smelt reduction tests are given in Table 5.

Table 5 - Analyses of metal and slag after smelt reduction

Pos.:	Textual description	Remarks	Unit	Test 2:		Test 3:
1	weight of the sample before heat treatment		[g]	484,00		536,00
2	sum of products after heat treatment		[g]	337,32		376,26
3	loss of weight after heat treatment		[%]	30,3		29,8
4	theoretic mass of Fe_{total} in sample		[g]	157,25		174,15
5	theoretic mass of Cr_{total} in sample		[g]	32,04		35,48
6	theoretic mass of Ni_{total} in sample		[g]	10,5		11,6
7	sum of Fe met in metallic products after heat treatment		[g]	145,36		156,74
8	sum of Cr met in metallic products after heat treatment		[g]	32,89		28,47
9	sum of Ni met in metallic products after heat treatment		[g]	6,92		7,51
10	sum of Fe as Fe2O3 in slag-like products after heat treatment		[g] (as Fe!)	8,02		9,03
11	sum of Cr as Cr2O3 in slag-like products after heat treatment		[g] (as Cr!)	5,36		6,32
12	sum of Ni as NiO in slag-like products after heat treatment		[g] (as Ni!)	0,49		0,8
13	total sum of Fe in products after heat treatment	Pos. 7 + Pos. 10	[g] (as Fe!)	153,38		165,77
14	total sum of Cr in products after heat treatment	Pos. 8 + Pos. 11	[g] (as Cr!)	38,25		34,79
15	total sum of Ni in products after heat treatment	Pos. 9 + Pos. 12	[g] (as Ni!)	7,41		8,31
16	percentage of Cr in metallic products	basis Pos. 14	[%]	86,0		81,8
17	percentage of Ni in metallic products	basis Pos. 15	[%]	93,4		90,4
18	percentage of Cr in slag-like products	basis Pos. 14	[%]	14,0		18,2
19	percentage of Ni in slag-like products	basis Pos. 15	[%]	6,6		9,6

From **Table 5** we can compare the input masses of Fe, Cr and Ni in the brick (lines 4,5,6) with the output in the metal phase (lines 7,8,9) to get an impression of the reduction yield. The too high Cr met in test 2 (line 8) is obviously due to analysis errors.

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Basic layout and performance of the TISCO plant

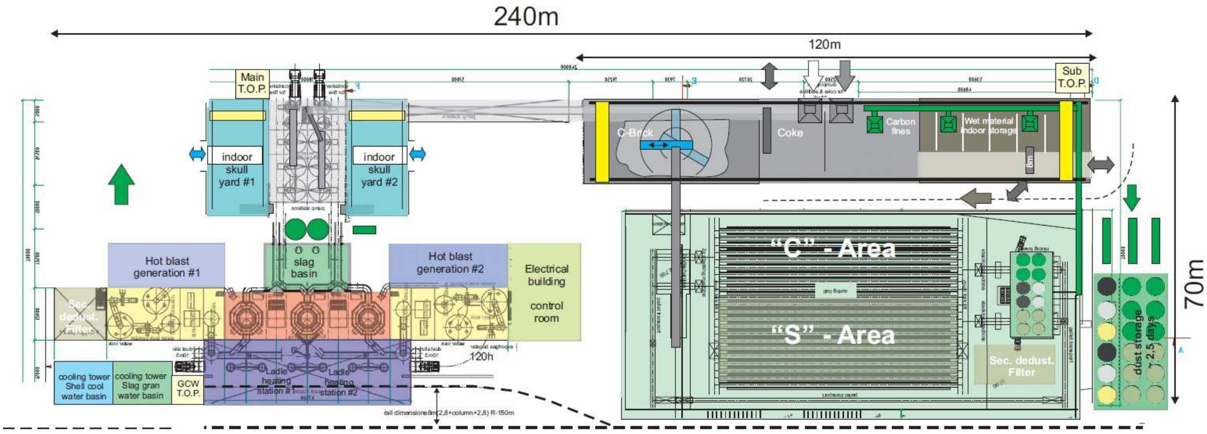

Figure 7 - OxyCup plant with two separate lines. One line for residues from stainless steel production and one line for residues from carbon steel production. From the 3 installed furnaces are only two in operation while the third is under maintenance.

The brick making area is divided in two parts "C" and "S" to avoid confusion with respect to the stainless and carbon steel residues. Both lines are equipped with wet gas cleaning lines that allow export of the clean process gas to the powerstation of the works. The two furnaces can process up to 2 x 45 t/h of bricks and skulls.
The produced hot metal and liquid iron alloy will be collected in rail bound laddles and partly added to the electric melting furnaces.
The plant is under construction and will start operation in the beginning of 2011.