

Characterisation of slag products obtained through reduction of stainless steelmaking slags

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Abstract

Slag from stainless steel production has been processed in a DC-furnace, equipped with a hollowed electrode. Most of the iron, chromium and nickel from the slag were recovered as a metal. The remaining slag was modified to a slag product.

This paper describes the investigation of the slag product with respect to the mineralogy, volume stability and leaching properties. From the results it is concluded that stainless steel slags can be converted into a stable inert slag product. Chromium leaching was effectively reduced and slag disintegration could be prevented with controlled slag additions.

Introduction

Slags from stainless steelmaking are by-products that are characterised by their content of valuable metals, especially chromium and nickel. The recovery of these elements in normal steelmaking processes is difficult. The use of these slags as mineral aggregates in the building industry is often hindered by a lack of volume stability and an insufficient environmental compatibility.

The scope of this work was to examine processed stainless steelmaking slags.

Slag from stainless steelmaking (EAF slag, converter slag and a mixed slag from magnetic separation) were smelted in a pilot plant DC electric arc furnace equipped with a hollowed electrode as shown in Figure 1. The slag was fed together with anthracite into the hollowed electrode. Following this treatment, most of the iron, chromium and nickel content of the original slag was reduced and recovered as a metallic product. During the reduction, controlled additions were used to modify the composition of the remaining slag and to improve the metal/slag separation.

The remaining slag was examined for use in two possible applications:

- Air-cooled slag stone, as mineral aggregates in the building industry.
- Water granulated slag, as replacement for cement in concrete.

Characterisation of slag products

Starting materials were taken from stainless steelmaking slags such as EAF slag, converter slag and a mix of different slag after magnetic separation, respectively (c.f. Table 1). Air-cooled slag from ten heats in the pilot plant DC electric arc furnace and the water granulated slag from two of these heats (no 8 and 9) were included in this study. About 30 kg of air-cooled slag from each heat were crushed, screened and divided into sub-samples. The chemical composition of the slag products was determined and the mineral composition was determined by XRD.

The swelling behaviour was tested using the steam test procedure and the content of free lime was determined using the DIN EN 1744-1 procedure. The environmental compatibility was tested by the leaching procedure, DIN 38414 (DEV-S4). The slag products were also examined using Scanning Electron Microscopy with EDS.

Water granulated slag from two of the heats were ground and tested as replacement for cement in concrete. The replacement of cement was done according to equivalent volume basis.

45 volume-% ground and granulated slag and 55 volume-% OPC (Ordinary Portland Cement) was mixed with water at a mass water/solid ratio of 0.27. This sludge was then tested in a calorimeter for 24 hours to examine the effect of slag addition on the early hardening of the cement.

The same slag/cement mixture (45 volume-% slag and 55 volume-% OPC) was mixed with water at a mass water/solid ratio of 0.50. Standard sand (DIN 196) was added to the cement paste (at a sand/cement-ratio of 3). Test specimens measuring 4×4×16 cm were prepared and aged up to 91 days. Strength testing was performed using the European Standard EN 196-1 procedure.

Reference tests (both calorimeter test and strength test) were carried out with quartz instead of granulated slag. Quartz in these tests is regarded as an inert material.

Results

The chemical composition of the slag before and after the reduction, i.e. the treatment in the DC EAF, (c.f. Table 2) shows a decrease of chromium oxide and total iron content, but also a change in basicity, CaO/SiO_2 . The main mineral components in the all air-cooled slags were Gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and various magnesium-calcium silicates such as:

- Akermanite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$)
- Monticellite ($\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$)
- Merwinite ($3\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$)

Air-cooled slag from two of the heats disintegrated (heat no 5 and 9). These slags have high basicities, 1.6 and 1.8, compared to the other slags (< 1.35). Different polymorphs of dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) were present in these two slags.

The steam test results shows a limited maximum expansion for the air-cooled slag (c.f. Figure 2). The volume expansion after 24 hours was measured to below 0.5% and the maximum expansion (theoretically when $t \rightarrow \infty$) below 2.5% for all samples. The free lime content of the slag was reduced from 0.5-2.7 wt-% to 0.2 wt-% or less for all samples, c.f. Table 3.

The analysis of the leachate, from the leaching tests of the air-cooled slags, shows a low concentration of chromium (c.f. Table 4). There is an obvious correlation between the pH and electrical conductivity versus the Ca content of the leachate (c.f. Figure 3). The leachate from the disintegrated slags (heat no 5 and 9) had a significant higher pH and Ca content. This is mainly due to the higher surface area of the fine-grained material.

The SEM examinations of the air-cooled slag products showed tiny metal droplets in the slag matrix. These droplets ranged in size from a few μm up to approximately $100\mu\text{m}$ and contained varying amounts of metallic iron and chromium but also titanium and silica were present, c.f. Figure 4.

The examination of slag as replacement for cement in concrete, was done using ground and water granulated slag from heat numbers 8 and 9. The calorimeter test of this slag in cement paste showed only minor differences compared with a quartz reference (c.f. Figure 5). This means the reactivity of the granulated slag is low within the first 24 hours and no harmful reactions had taken place during this time.

The compressive strength was tested after 1, 28 and 91 days, respectively (c.f. Figure 6). The test shows a significant improvement of the long-term (of 91 days of ageing) compressive strength compared to the quartz reference.

Discussion

The chromium content of the leachate for the treated slag, compared with the original slag, was significantly lower. But the total chromium content of the slag did not decrease to the same extent. This can be explained by the presence of metal droplets with significantly high chromium content left in the slag after treatment. This suggests that the total chromium content of the slag could be further decreased by an improved metal/slag separation in the DC-arc furnace process.

The testing of the air-cooled slag shows improved volume stability. The measured volume increase and free lime content in the slag meet the requirements for maximum volume increase ($< 5 \text{ vol-\%}$) and maximum free lime ($< 7 \text{ wt-\%}$) that have been suggested for fresh steel slag (i.e. not weathered) in unbound layers of roads [2].

The disintegrated slags (i.e. the slags from heat numbers 5 and 9 and the original AOD slag) did contain $2\text{CaO}\cdot\text{SiO}_2$. The disintegration is caused by the transformation from the β - to the

γ -modification of the dicalcium-silicate on cooling down. By additions of sand the slag ratio could be reduced preventing the formation of $2\text{CaO}\cdot\text{SiO}_2$ and thus the disintegration. The leaching test shows also that the disintegration of slag promotes the leaching of slag and therefore should be avoided.

By reduction of chromium the leaching of the treated slag becomes comparable with slags from production of carbon steel in ordinary electric arc furnace steel making. The leaching test of the air-cooled slag meets the requirements for electric arc furnace slag according to the regulations in Nordrhein-Westfalen, Germany (pH: 10-13, Conductivity_{max}=500 mS/m and $\text{Cr}^{\text{IV}}_{\text{max}} = 0.3 \text{ mg/kg}$) [3].

The results from the cement testing indicate that the ground and granulated slag have a latent hydraulic effect. This effect is characterised by an improved strength of the cement made of slag together with OPC, especially over a long-term basis. To some extent the ground granulated slag should be capable to replace OPC without loss of quality. In this sense it might be compared to ground granulated blast furnace slag used in the production of blast furnace cements. To determine whether the slag can be used as slag cement or not, further testing must be carried out.

Conclusions

This investigation indicates that the treatment of stainless steelmaking slag in the DC arc furnace, equipped with a hollowed electrode, improves the volume stability of the slag as well as having sufficient environmental compatibility.

The treated and air-cooled slag can be utilised as a mineral aggregate in the building industry. The leachability of the air-cooled slag and the volume properties of this slag meet the requirements in building industry. To prevent slag disintegration the results indicate that the slag basicity should be kept low.

The study also indicates that the chromium yield from the reduction process can be improved if there is an improvement in slag-metal separation. This would also decrease the total chromium content of the slag.

The study of the water-granulated slag indicates that the slag can be utilised in a similar way as granulated blast furnace slag cement. The granulated and ground slag has a latent hydraulic effect.

References

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3. Schriftenreihe der Forschungsgemeinschaft Eisenhüttenschlacken e.V., "Eisenhüttenschlacken", Duisburg, Germany, (1996), p.116

Figures

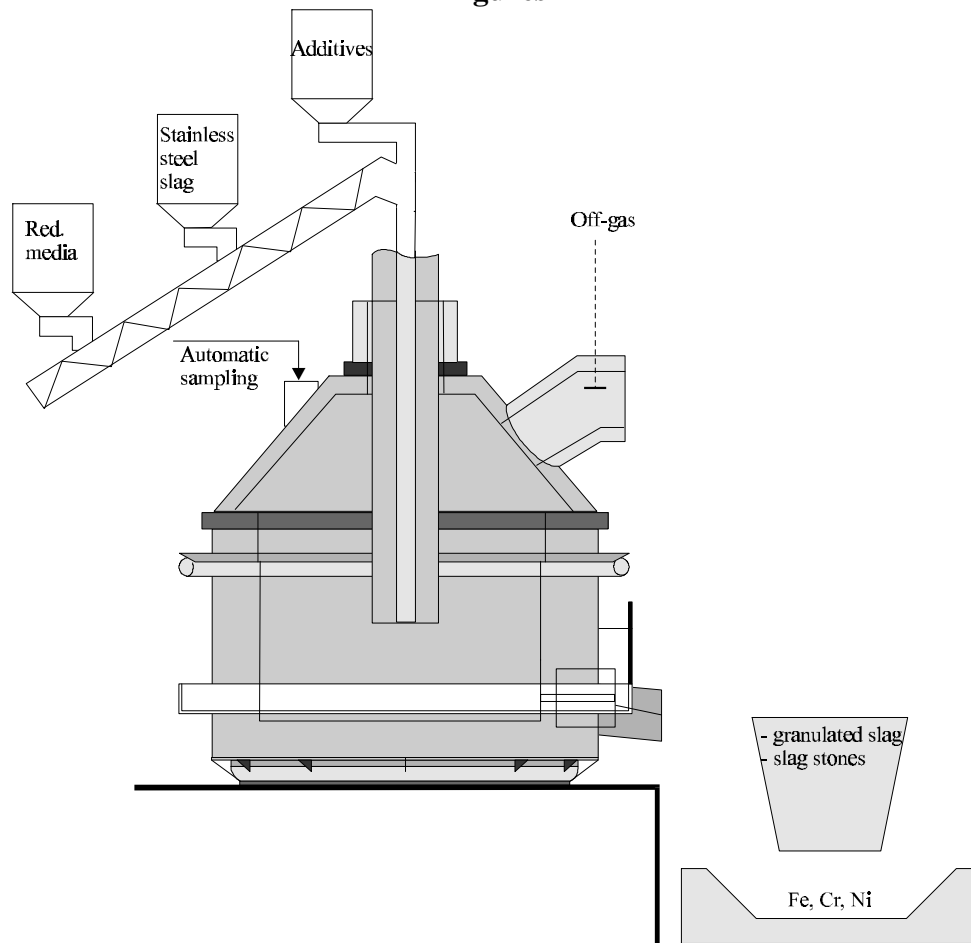


Figure 1. The slag reduction concept [1]

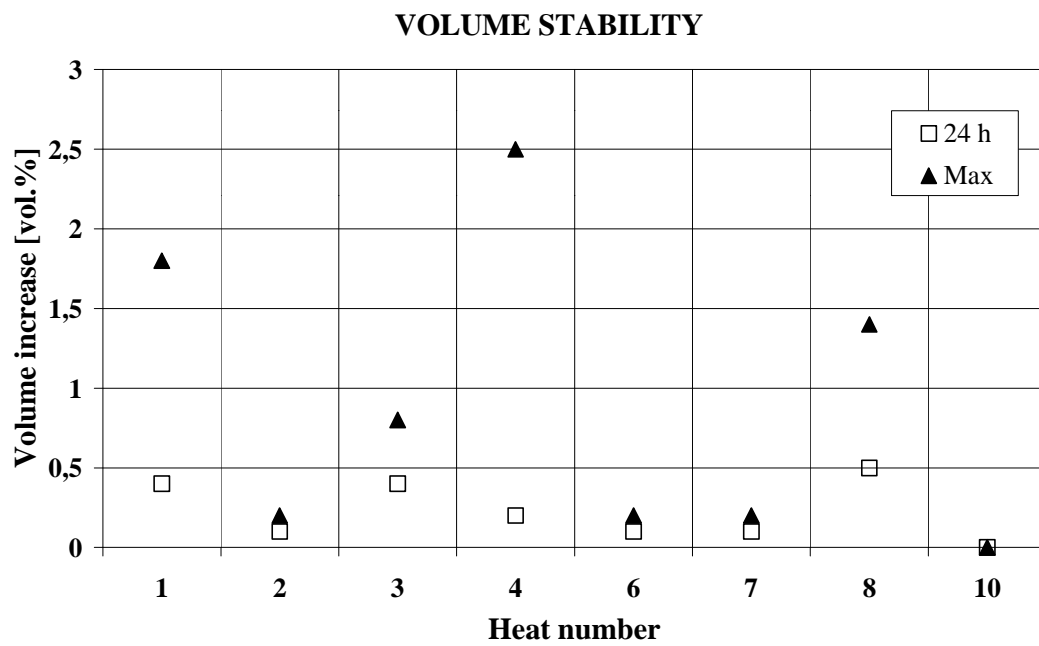


Figure 2. Steam test results of air-cooled slag products.

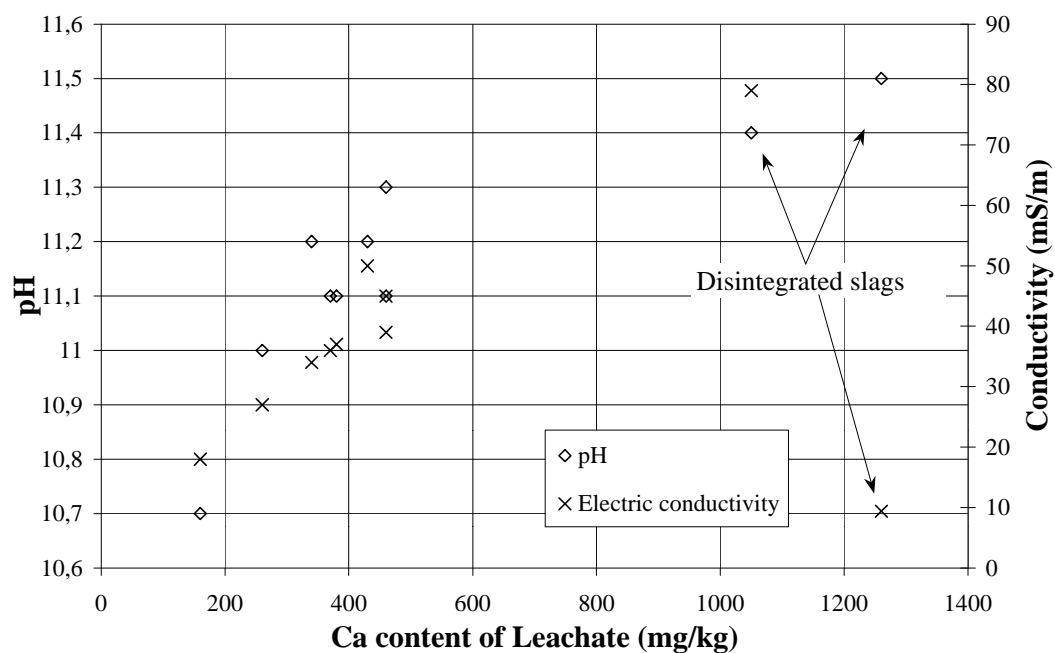


Figure 3. Ca content versus pH and electric conductivity of leachate.

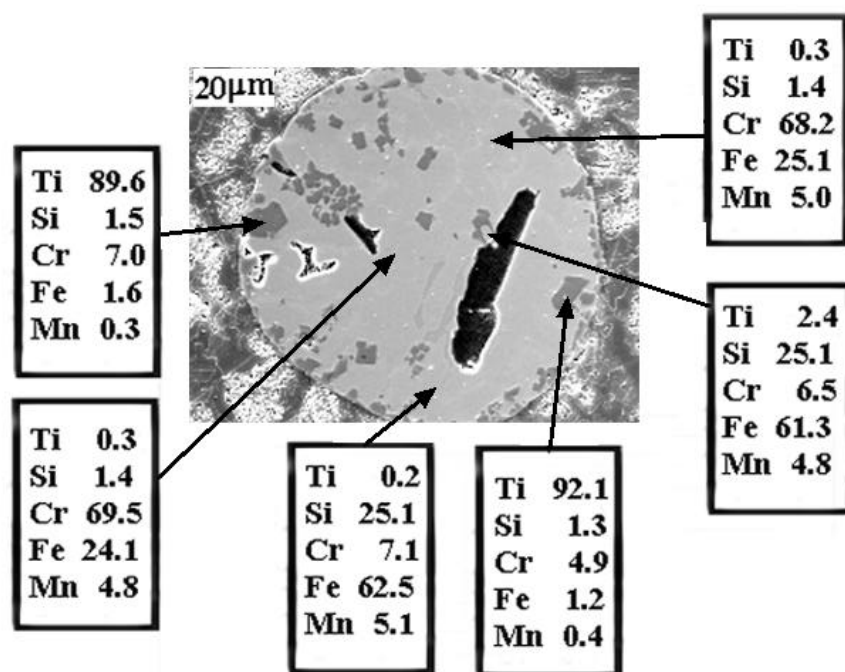


Figure 4. Metal droplet in slag from heat number 5 (in wt-%, normalised analyse)

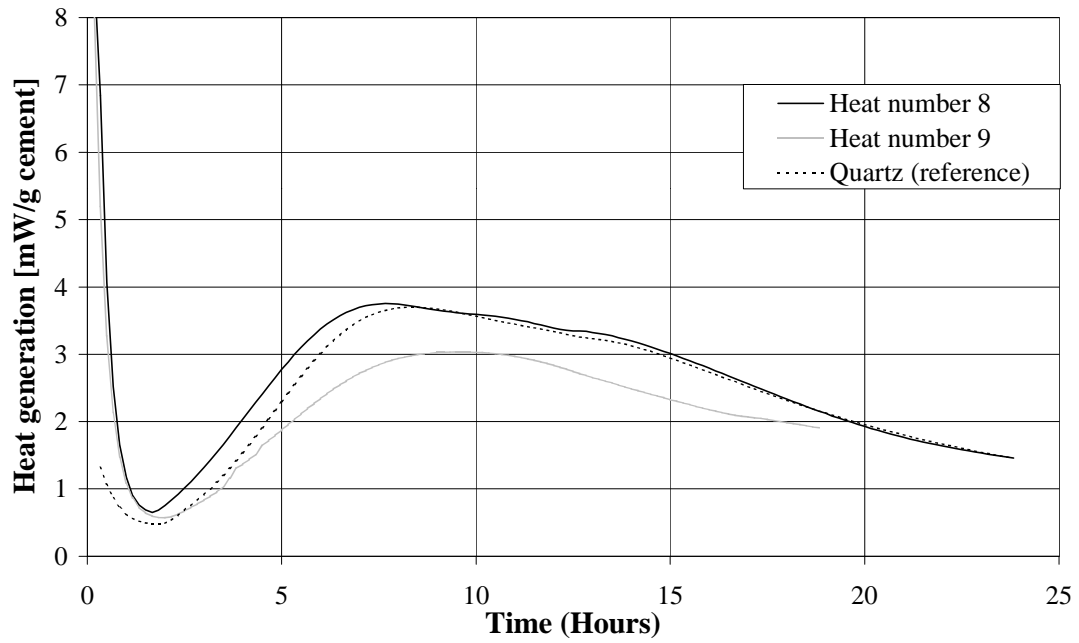


Figure 5. Heat generation in calorimeter test.

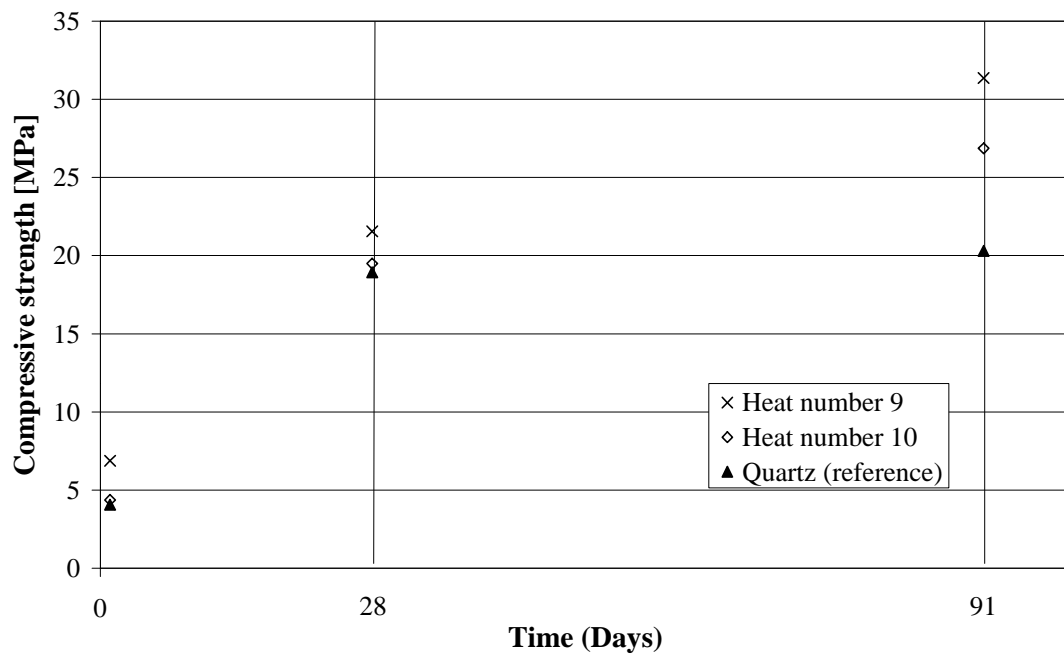


Figure 6. Compressive strength of cement

Tables

	Heat number									
	1	2	3	4	5	6	7	8	9	10
Mixed slag ¹	X	X	X							
EAF slag				X	X	X	X	X	X	
Converter slag										X
Additions (except for CaO, MgO and anthracite)			Pig iron		Pig iron	Mill scale	Bauxite	Sand	Mill scale	Mill scale

Table 1. Original slag used in the different heats.

		HEAT NUMBER									
		1	2	3	4	5	6	7	8	9	10
SiO ₂	Before	28.2			33.7						28.0
	After	32.7	31.3	35.4	33.4	33.2	34.2	34.2	24.1	33.6	30.0
CaO	Before	37.0			39.0						54.9
	After	40.4	42.7	44.6	39.9	54.6	47.2	31.7	42.9	54.5	42.6
Al ₂ O ₃	Before	5.65			3.75						3.02
	After	10.6	10.6	4.65	8.06	5.54	4.98	27.7	7.0	3.9	8.1
MgO	Before	11.1			7.8						6.6
	After	11.6	10.2	9.7	13.6	4.4	6.6	5.1	7.0	3.9	8.1
Cr ₂ O ₃	Before	3.47			7.0						0.73
	After	0.29	2.06	0.6	0.62	0.23	0.62	1.79	0.4	0.35	0.85
Fe-tot	Before	1.11			1.28						0.38
	After	0.19	1.32	0.31	1.42	0.27	0.38	2.24	0.95	0.91	1.7
CaO SiO ₂	Before	1.31			1.16						1.96
	After	1.24	1.36	1.26	1.19	1.64	1.38	1.32	1.28	1.82	1.2

Table 2. Chemical composition of original slag and slag products (in wt-%).

		HEAT NUMBER									
		1	2	3	4	5	6	7	8	9	10
Before treatment		0.5			1.48						2.7
After treatment		<0.2	<0.2	<0.2	<0.2	0.2	<0.2	<0.2	<0.2	0.2	<0.2

Table 3. Treatment effect on amount of free lime in slag (wt-%).

¹ Mixed slag (EAF slag, converter slag and ladle slag) from stainless steelmaking after magnetic separation.

		HEAT NUMBER									
		1	2	3	4	5	6	7	8	9	10
Cr (mg/kg)	Before	13.4			1.1						0.9
	After	<0.1	<0.1	<0.1	0.1	0.1	0.1	<0.1	<0.1	0.1	<0.1
pH	Before	11.8			12.4						12.4
	After	10.7	11.2	11.1	11	11.5	11.2	11.1	11.1	11.4	11.3
Cond. (mS/m)	Before	166			770						814
	After	18	50	37	27	9.4	34	39	36	79	45
Ca (mg/kg)	Before	1460			8230						8430
	After	160	430	380	260	1260	340	460	370	1050	460

Table 4. Leachate analysis of slag before and after treatment
(mg element per kg slag)