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Aqueous Leachate from Electric Furnace Slag

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In manufacturing manganese and carbon steel in the basic electric arc furnace, 70 to 80 kg of slag per tonne of steel is produced, whereas the grey cast production results in 30 to 40 kg of slag per tonne of grey cast. Such large slag volumes require special care for their disposal at landfills near steel and rolling mills. It is therefore necessary to examine the chemical stability of slag under various conditions.

The paper reports examinations of the chemical and phase composition of slag, as well as the number of anions and cations. The number of anions and cations in water eluates was determined in order to define the influence of such material on the environment. The phase composition of slag was determined by the X-ray diffraction method. Eluated anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-}) were determined by ion-chromatographic analysis. Eluated cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were established by spectrometric atom absorption.

Changes in pH, conductivity and chemical composition of water eluates were monitored for 96 hours. The results have shown that the examined slag material could, with regard to its chemical and phase composition, constitute a stable Fe-Mn-Ca silicate material. However, elution of the examined components, along with the change in conductivity and pH value, implies that slag is not chemically inert and that therefore the problem of slag disposal has to

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be approached paying special attention on its potential impact on the environment.

Key words: electric furnace slag, slag phase composition, anions chromatographic analysis, chemical stability of slag

INTRODUCTION

Large quantities of electric arc slag are produced in the process of making steel and grey cast in electric arc furnaces. The function of slag is to remove harmful substances from the liquid metal, to take on valuable alloying additives, and to protect steel.[1–3]

85% of slag and dusts are sent to a secondary facility to recover valuable metals.[4] The slag grades obtained in steel production are very suitable for road construction material, if the adequate volume stability is secured. Slag material obtained during high-manganese steel production can be recycled in the manufacture of the same type of steel. Recent research has implied that electric furnace slag can be used as an additive in cement production.[5–8] Some electric furnace slag is placed on depots in the vicinity of steel mills and foundries. Large quantities of slag require a special approach to the disposal and storage of this material, which can pollute the air, water and soil as well as disfigure the environment. A detailed characterization of slag is therefore absolutely necessary.

Earlier investigations have shown a low content of radionuclides and toxic metals.[7] Several authors have examined the effects of leaching on slag samples. Leaching tests (using deionized water, acetic acid/sodium acetate pH 4.74 buffer solution, and controlled pH 4 nitric acid solution) were performed in order to register the leachability and pollution potentials. Different pH-values were established in these tests in order to control the leachability of Na, K, Ca and Mg.[9–10] The purpose of the leaching test was to confirm slag safety.[11] Many experiments showed that some elements, *e.g.* potassium, are easily leached. Electric conductivity is changed along as well.[12–13]

The anions, which are relevant because of their impact on the environment (F^-, Cl^-, Br^-, NO_3^-, NO_2^- and SO_4^{2-}), were determined by the ion-chromatographic method. Eluted anions were detected using a combination of ion exchange columns and conductivity detection. The chromatographic approach is simple and versatile and has the additional advantage of being applicable to a wide range of concentrations (1 ppm – 50 ppm).[14–18]

This paper deals with detailed investigations of the reactions between the slag and eluents, with anion determination by ion chromatography and cation determination by atomic absorption spectrometry.

EXPERIMENTAL

Samples

Five characteristic samples of electric furnace slag were used to define the chemical composition, phase composition and elution parameters.

The samples were taken during the production of 0545 low carbon steel and Hadfield steel, as well as the slag from the production of grey cast iron. The samples were marked with numbers 1 to 5 and are presented in Table I. Samples 1 to 5 were taken with a spoon onto a plate and cooled with water. Cold samples (294 K) were ground and homogenized for 150 minutes in a Herzog vibration mill. Successive quartering and crushing of cold samples provided 100 g of each sample.

TABLE I

Samples of electric furnace slag

EFS Sample	Type of steel	*T*/K of EFS
1	0545 low carbon steel	1833
2	0545 low carbon steel	1903
3	grey cast iron	1673
4	Hadfield steel	1883
5	Hadfield steel	1763

EFS – electric furnace slag

All samples were dried for 2 hours at 378 K and stored in a desiccator above silica gel.

Procedures

Investigation into the chemical composition of slag was carried out by means of a classical chemical analysis.[19] The sulphur content was determined by burning down using an automatic analyzer for sulphur and carbon C, S-444 (Leco).

Prior to phase composition determination, the samples were ground and homogenized in a Spex Mixer Mill tungsten – carbide grinding container for 20 minutes.

The slag phase composition was determined with a diffractometric system (Phillips) by the counting technique and Cr$K\alpha$ radiation in the angle area from 5 to 144°, 2θ, at the observation rate of 1 °C/min; and the susceptibility 1×10^4. Diffractographs were analyzed by comparison, using the JCPDS data (Joint Commitee on Powder Diffraction Standards) published by Narita.[20]

Conductivity, pH-value, anion and cation concentrations of eluates were examined on samples obtained by shaking 1 g of a slag sample with 25 mL of redistilled water. Samples were equilibrated for 1 hour, 24 hours, 48 hours, 72 hours, and 96 hours. Samples were shaken on a Digital incubator shaker (Innova 4000/4080).

After shaking, the samples were filtered through a 0.45 μm filter FP 030/2 (Schleicher, Germany), diluted to 100 mL, and analyzed.

Conductivity was measured with a conductivity meter MA5969 (Iskra) and the pH-value was measured with pH meter MA 5730 (Iskra).

Concentrations of anions in aqueous eluents were determined by the ion chromatrography method. The anion exchange ion chromatography was performed using a 690 Ion Chromatograph (Metrohm) with IC anion column PRP-X100.

Sample solutions must always be filtered through a 0.45 μm membrane filter.

As a large concentration of dissolved cations can perturb the base line (Figure 1) for sensitive analyses, they should be removed with a cation exchanger in Na-form.

Cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) were analyzed using an atomic absorption spectrometer 3110 (Perkin Elmer).

Steps in the procedures

Experimental condition (Ion Chromatograph):

Eluent: 2.5 mmol/L phthalic acid
5% (V/V) acetonitrile, pH = 5.0
Flow: 1.5 mL/min
Pressure: $20 \cdot 10^5$ Pa
Injected volume: 100 μL
Full scale: 5 μS/cm

Experimental condition (Atomic Absorption Spectrometar):

Resonant line for calcium: 422.7 nm
Resonant line for magnesium: 285.2 nm
Resonant line for potassium: 766.5 nm
Resonant line for sodium: 589.0 nm
Mixture of gases in the burner: air and acetylene
Air operating pressure: $4 \cdot 10^5$ Pa
Acetylene operating pressure: $1 \cdot 10^5$ Pa
Integration time: 2 sec
Radiation sources: Ca, Mg, K and Na hollow cathodes.

RESULTS AND DISCUSSION

The electric furnace slag is a material that requires special investigation in order to examine its influence on the environment. The primary task is to test slag stability. The results of the quantitative chemical analysis are shown in Table II. Minor deviations of the chemical composition of the examined slag samples from reference data resulted from the change in the production process, *i.e.* in charge quality.[5]

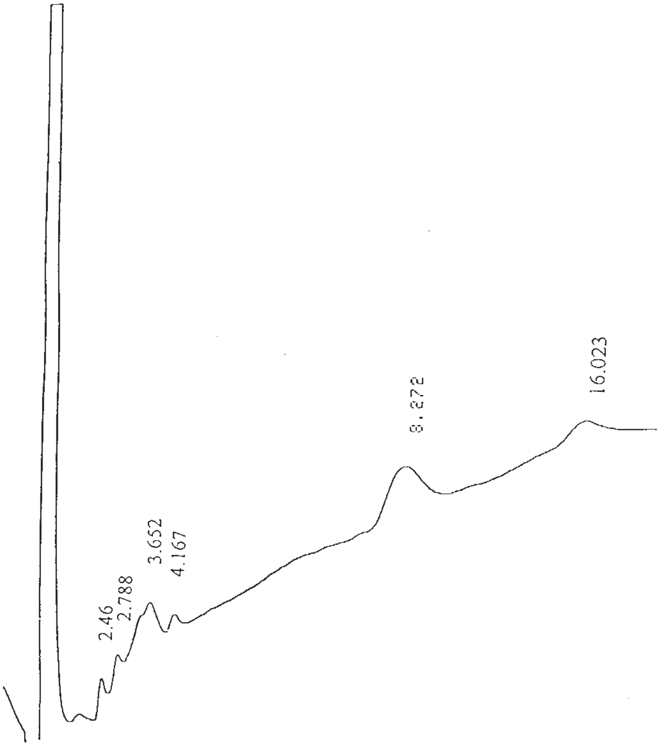


Figure 1. Chromatogram of sample 1 before treating with strong acidic cation exchanger.

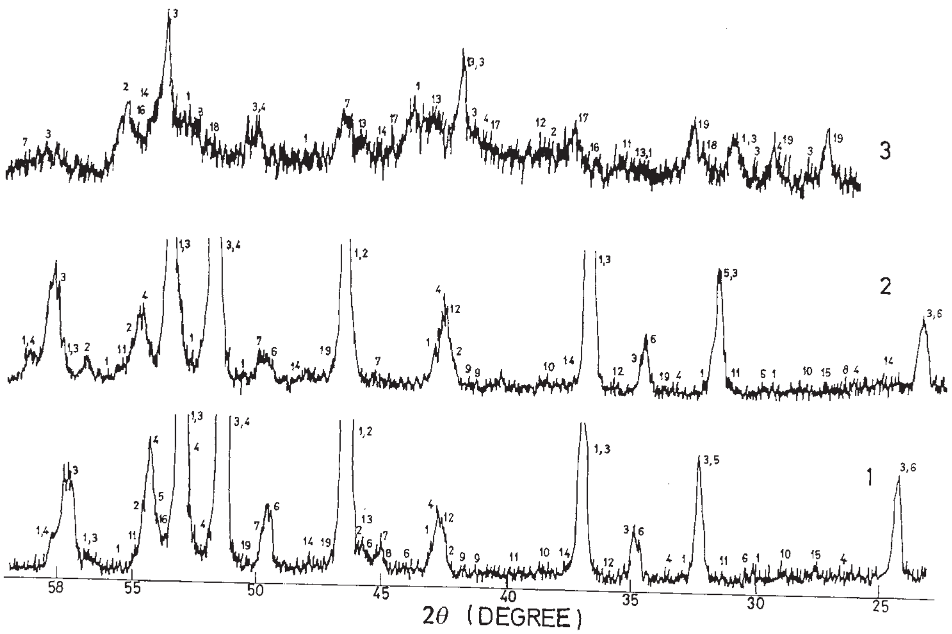
The results of X-ray diffraction phase analysis of slag samples are given in Figures 2 to 6. (Characteristic sections of diffractographs are shown in the figures).

The basis of electric furnace slag in samples 1, 2, and 3 is primarily a mixture of Ca-Fe-O phases having unspecified formula and calcium-magne-

TABLE II

Mass fraction /% of electric furnace slag

Sample	SiO_2	Fe_2O_3	FeO	CaO	MgO	Mn_2O_3	Al_2O_3	P_2O_5	S	K_2O	Na_2O
1	32.48	9.26	8.48	21.06	10.43	14.02	3.20	0.031	0.010	0.59	0.24
2	27.54	0.49	7.11	26.74	22.84	9.71	4.52	0.019	0.015	0.60	0.23
3	37.52	6.75	4.96	20.02	21.10	7.45	0.92	0.074	0.083	0.88	0.27
4	31.25	2.00	0.00	13.21	16.24	35.97	0.00	0.048	0.010	0.85	0.26
5	32.22	2.74	0.00	13.10	17.45	33.24	0.00	0.045	0.010	0.62	0.24



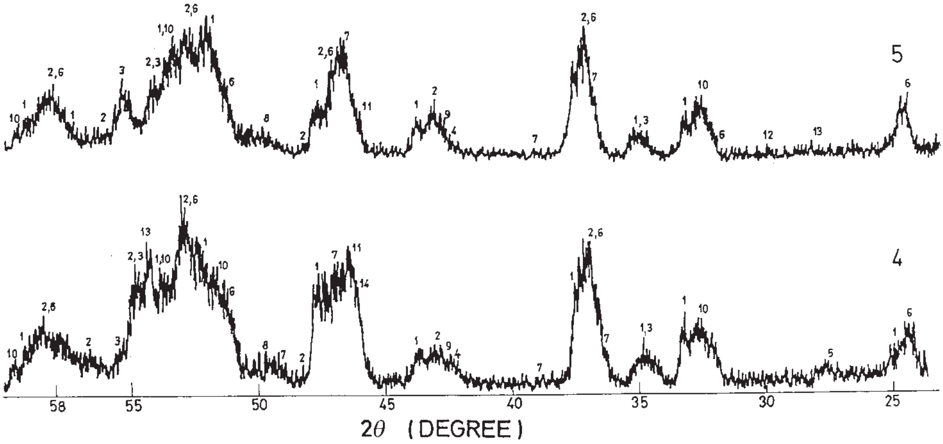
Figures 2–4. X-ray diffraction patterns of average electric furnace slag samples 1–3.

Identified phases:
1: $2MnO \cdot SiO_2$; 2: $MgSiO_3$; 3: $CaO \cdot MgO \cdot SiO_2$; 4: Ca-Fe-O (mixture of unspecified formula); 5: MnO_2; 6: $8CaO \cdot 3SiO_2 \cdot 3H_2O$; 7: $\alpha 2CaO \cdot SiO_2$; 8: Mn_3O_4; 9: $CaO \cdot Al_2O_3 \cdot 2SiO_2$; 10: βSiO_2; 11: αSiO_2; 12: $\alpha 3CaO \cdot 2SiO_2$; 13: $MnSiO_3$; 14: $2FeO \cdot SiO_2$; 15: FeO; 16: $CaMgSi_2O_7$; 17: $2CaO \cdot MgO \cdot 2SiO_2$; 18: $(Mn, Mg)_2SiO_4$; 19: $CaO \cdot MgO \cdot 2SiO_2$

sium silicates. Other identified phases, as compared to the fundamental phases, were detected in a smaller or considerably smaller concentration.

The electric furnace slag in samples 4 and 5 primarily involves manganese-oxides silicate phases, which agrees with the references.[21] The X-ray powder diffraction analysis has shown that the slag consists of stable Fe-Mn-Ca silicates.

The results of leaching effect tests are given in Table III. Table III shows that the material that has been proven chemically and X-ray stable is not entirely stable. Extraction with water caused dissolution of some components and hydrolysis. In all samples, we observed that the pH-value, conductivity, and cation concention (Na^+, Mg^{2+}, and Ca^{2+}) increased with time, while the concentration of K^+ retained similar values in the course of time (samples 1, 4 and 5) or it showed a minor decrease after 24 hours as compared to 1 hour; still, approximately identical values were retained to the



Figures 5–6. X-ray diffraction patterns of average eletric furnace slag samples 4–5.

Identified phases:
1: (Mn, Mg)$_2$SiO$_4$; 2: 2MnO·SiO$_2$; 3: 2MgO·SiO$_2$; 4: MgSiO$_3$; 5: Mn$_3$O$_4$;
6: CaO·MgO·SiO$_2$; 7: βMnSiO$_3$; 8: α2CaO·SiO$_2$; 9: α3CaO·2SiO$_2$; 10: MnO$_2$;
11: MnSiO$_3$; 12: αSiO$_2$; 13: CaO·MgO·2SiO$_2$; 14: Mg$_3$Si$_4$O$_{10}$(OH)$_2$

TABLE III

Monitoring of leaching effects on samples of electric furnace slag during 96 hours

EFS 1	1 hour	24 hours	48 hours	72 hours	96 hours
pH	6.25	6.78	6.82	6.97	7.06
conduct. /μScm^{-1}	15.60	18.50	29.50	32.30	41.60
Na$^+$, mg/100mL	0.255	0.272	0.294	0.334	0.336
K$^+$, mg/100mL	0.097	0.092	0.094	0.106	0.108
Ca^{2+}, mg/100mL	0.112	0.118	0.128	0.142	0.156
Mg^{2+}, mg/100mL	0.038	0.039	0.050	0.0536	0.054
F$^-$, mg/100mL	0.177	0.217	0.204	0.378	0.605
Cl$^-$, mg/100mL	0.154	0.124	0.118	0.111	–
SO$_4^{2-}$, mg/100mL	0.025	0.076	0.070	0.070	0.070
EFS 2	1 hour	24 hours	48 hours	72 hours	96 hours
pH	10.67	10.83	10.55	11.06	11.13
conduct. /μScm^{-1}	135.30	141.20	150.00	162.00	169.00
Na$^+$, mg/100mL	0.075	0.079	0.094	0.105	0.130
K$^+$, mg/100mL	0.051	0.035	0.031	0.037	0.038
Ca^{2+}, mg/100mL	1.032	1.172	1.230	1.310	1.450
Mg^{2+}, mg/100mL	0.016	0.016	0.018	0.018	0.019
F$^-$, mg/100mL	–	0.335	0.460	0.511	0.710
Cl$^-$, mg/100mL	0.086	0.031	0.033	0.039	–
SO$_4^{2-}$, mg/100mL	0.046	0.028	0.053	0.030	0.045

TABLE III (continued)

EFS 3	1 hour	24 hours	48 hours	72 hours	96 hours
pH	6.77	7.02	7.65	7.69	7.73
conduct. /μScm^{-1}	13.80	17.61	18.50	19.40	19.89
Na^+, mg/100mL	0.114	0.116	0.132	0.135	0.136
K^+, mg/100mL	0.093	0.069	0.068	0.067	0.068
Ca^{2+}, mg/100mL	0.128	0.131	0.150	0.161	0.173
Mg^{2+}, mg/100mL	0.029	0.050	0.063	0.065	0.069
F^-, mg/100mL	0.3663	0.226	0.298	0.478	0.604
Cl^-, mg/100mL	0.031	0.027	0.027	–	–
SO_4^{2-}, mg/100mL	0.016	0.016	0.016	0.018	0.012

EFS 4	1 hour	24 hours	48 hours	72 hours	96 hours
pH	6.27	6.85	6.98	7.32	7.46
conduct. /μScm^{-1}	10.40	12.01	16.89	18.17	18.95
Na^+, mg/100mL	0.076	0.121	0.126	0.127	0.128
K^+, mg/100mL	0.086	0.086	0.075	0.080	0.082
Ca^{2+}, mg/100mL	0.042	0.053	0.102	0.132	0.143
Mg^{2+}, mg/100mL	0.018	0.038	0.050	0.061	0.063
F^-, mg/100mL	0.1698	0.274	0.228	0.806	0.861
Cl^-, mg/100mL	0.029	0.026	0.024	–	–
SO_4^{2-}, mg/100mL	0.021	0.021	0.019	0.020	0.019

EFS 5	1 hour	24 hours	48 hours	72 hours	96 hours
pH	6.85	6.95	7.08	7.36	7.45
conduct. /μScm^{-1}	13.12	13.94	17.80	19.31	20.69
Na^+, mg/100mL	0.098	0.102	0.106	0.111	0.115
K^+, mg/100mL	0.059	0.057	0.058	0.059	0.060
Ca^{2+}, mg/100mL	0.128	0.130	0.142	0.151	0.160
Mg^{2+}, mg/100mL	0.055	0.057	0.065	0.066	0.067
F^-, mg/100mL	0.220	0.224	0.230	0.915	0.346
Cl^-, mg/100mL	0.024	0.020	0.015	0.315	–
SO_4^{2-}, mg/100mL	0.072	0.057	0.056	0.048	0.050

end (samples 2 and 3). The change in conductivity implies that interactions were not completed after 96 hours. Further investigations should deal with the elution time extention and change of elution agents (rain, acid rain, waste water, *etc.*).

Accurate anion determination in complex matrices continues to be one of the most challenging areas in analytical chemistry. Computer simulation and experimental investigations were applied to examine the behaviour of anions and six system peaks in ion exchange chromatography.[22]

Anions from eluates hydrolize and this causes the change of the pH-value and conductivity. In the course of time, in the slag contact with water, the concentration of chlorides decreases due to the parallel sedimentation of poorly soluble chlorides.

In the course of elution, some unexpected components emerged (traces of nitrates and fluorides), which presumably came from the raw materials used in the production process. For example, fluoride is found in slags in the form of CaF_2 (2–5%), which is added to improve the viscosity and lower the melting point. The concentration of fluorides increases with time. No traces of nitrites, bromides or nitrates were found in the eluates.

Although elution effects also depend on the type of material, further investigations are required in order to accurately determine the inter-dependance between physical and chemical properties and leachate effects of eluates.

CONCLUSION

Electric furnace slag has a chemical and mineral composition that should imply the stability of this multi-component material. Regardless of whether the slag is disposed of or used for some purpose, care must be taken of the consequences that might arise from its affect on the environment.

Chemical and X-ray analyses have shown that slag is a Fe-Ca-silicate material. The results of spectrometric atomic absorption, ion chromatography, change in pH value and conductivity indicate that slag has been dissolved and water eluates have reacted with the environment during extraction.

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SAŽETAK

Izluživanje elektropećne troske

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U baznoj elektrolučnoj peći tijekom procesa proizvodnje manganskog i ugljičnog čelika nastaje 70 do 80 kg troske po toni čelika, a u procesu proizvodnje sivog lijeva 30 do 40 kg troske po toni sivog lijeva. Tako nastale velike količine troske zahtijevaju posebnu brigu pri odlaganju na deponije u blizini čeličana i ljevaonica. Stoga je potrebno ispitati kemijsku stabilnost troske u različitim uvjetima.

U radu su provedena ispitivanja kemijskog i faznog sastava troske te sadržaja aniona i kationa u eluatima troske da bi se odredio utjecaj takvog materijala na okoliš. Fazni sastav troske određen je metodom difrakcije rentgenskih zraka. Eluirani anioni (F^-, Cl^-, NO_2^-, Br^-, NO_3^- i SO_4^{2-}) određeni su ionskom kromatografijom, a eluirani kationi (Na^+, K^+, Ca^{2+} i Mg^{2+}) metodom atomske apsorpcijske spektrometrije. Promjena pH, vodljivosti i kemijskog sastava eluata promatrana je tijekom 96 sati.

Rezultati su pokazali da bi ispitivane troske prema kemijskom i faznom sastavu bile stabilan Fe-Mn-Ca-silikatni materijal. Međutim, elucija ispitivanih komponenata, uz promjenu vodljivosti i vrijednosti pH upućuje da troska nije kemijski inertna. Potreban je poseban pristup problemu odlaganja troske zbog mogućeg utjecaja na okoliš.