Original Scientific Paper

Ion Chromatographic Analysis
of Anion from Slag Elution

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Anions from blast furnace slag (F^-, Cl^-, Br^-, NO_3^-, NO_2^- and SO_4^{2-}) significantly influence the environment, human health, and the stability of structures. Particular attention is paid to reactions between the slag and the solution of the anions in question (of defined concentration) in the duration of 1 hour to 30 days.

The anions were determined by means of the ion chromatographic analysis modified for different proportions of anions in eluents.

The results of elution within reactions between slag and media point to the inertness of the system. The fluoride saturation factors of the system were experimentally determined and calculated with the help of distribution coefficients.

INTRODUCTION

Blast furnace slag is the most commonly used secondary raw material in the production of cements. Since slag from Željezara Sisak could be used in civil engineering and perhaps have some other applications, an investigation of its chemical, radiochemical and physical properties has been carried out. Blast furnace slag can reduce the cost of concrete and provide such benefits as reduced heat of hydration, resistance to sulphur attack, and inhibition of the alkali-aggregate reaction and even strength enforcement.[1,2,3,4]

Use of secondary raw materials, especially the blast furnace slag, can be dangerous to health, since some components, such as heavy metals and radioactive substances, tend to accumulate in them.

In 1956, B. Hulhrist published for the first time the radiation exposure data in Swedish homes. The radioactivity in building materials came mostly from the uranium, and thorium series and from natural potassium.[5-9] Legal provisions regulate the quantity of radioactive components in materials used in civil engineering.[10]

Besides the production of blast furnace Portland cements, Portland cements, cements, bricks and admixtures to mortar for civil engineering, it is also known that the slag, purified in a special way, can be used for the production of packing glass[11] and chromatographic bases.[12]

The demand for the determination of anions (F^-, Cl^-, Br^{-1}, NO_3^-, NO_2^- and SO_4^{2-}) in a variety of aqueous environments is rapidly increasing and, as a result, there is an expanding need for automated or semiautomated analyses of chemical plant streams, and environmentally important waters such as waste streams, rivers, lakes or fluids of biological interest such as blood, urine, *etc.* There are many examples of the continual need for routine analyses of common species such as anions. Ion exchange resins have the well known ability to provide excellent separations of ionic species, and there are a number of instances where ion exchange chromatography has been successfully applied.[13-17] The chromatographic approach is simple and versatile and has the added advantage of being applicable to a wide range of concentrations (1 ppm – 50 ppm).[18]

This paper deals with detailed investigations of the reactions between the slag and eluents, reactions of adsorptions or the ion exchange of F^-, Cl^-, Br^-, NO_3^-, NO_2^- and SO_4^{2-} in the slag-medium system, with anion determination by ion chromatography.

EXPERIMENTAL

In the experimental part, the chemical, radiochemical parameters and elution parameters of the blast furnace slag samples were observed during a period of five months.

Apparatus

The sulphur content was determined using the automatic analyzer for sulphur and carbon DB 64 of »LEKO« Co.

The gamma spectrometry investigation was carried out by means of Ge(Li) detector $\varepsilon = 15\%$ HWFM = 1.9 KeV at 1.33 MeV. The 4 K Canal analyzer Camberra, Series 10, directly connected to an Apple II computer with an appropriate program was used in investigations.

The slag phase composition was determined using a Phillips diffractometric system by the counting technique and CoK_α radiation in the angle area from 5 to 125°, 2θ, at the observation rate of 1°/min; 2°/min; and the susceptibility 1×10^3; 2×10^3.

The anion exchange ion chromatography was performed using an Ion Chromatograph 690 (Metrohm, Switzerland) with IC anion Column Super Sep and 697 IC pump. The anion exchange separator column system was coupled to high-capacity. The conductivity detector followed the two columns. The chromatogram was processed on a C-R5A Chromatopac by two methods; calibration with internal and external standards, respectively.

Reagents

All reagents were of the highest available purity and demineralized water was used for the dilutions and washings. All eluents were filtered through a 0.45 μm filter FP 030/2 (Schleicher, Germany). The solvent was degassed and no particulate matter was present. All glassware was soaked in a 10% hydronitric acid and rinsed copiously with high purity water prior to use.

Samples

In every shift (3), after the first pig iron tapping was made, a certain quantity of liquid slag was taken and cooled off with water. When cooled, the slag was ground below 100 μm in a »HER-ZOG« Co. vibration mill. The samples (approximately 50 g) were made up of ground slag (from every shift when the first iron notch was made). The average daily quantity of taken slag was 150 g.

The average monthly sample used in the experimental phase was made up of 30 average daily samples (previously homogenized in a »WEDEG« Co.) and divided into four parts for that particular month.

All samples were dried for 2 hours at 105 °C and stored in a desiccator above silica gel. The samples were marked by numbers 1–5 and were taken in the period from April to August 1991.[19]

Procedures

Investigation of the chemical composition of slag was carried out by means of a classical chemical analysis.[20] The sulphur content was determined by burning down using an automatic analyzer. The results are shown in Table I.

TABLE I

Mass fractions/% of blast furnace slag

Sample number	SiO_2	Al_2O_3	CaO	MgO	FeO	MnO	S	$\dfrac{n(CaO)}{n(SiO_2)}$	$\dfrac{n(CaO+MgO)}{n(SiO_2)}$
1	36.60	11.50	36.01	5.97	1.07	3.42	1.00	0.98	1.15
2	36.08	12.00	40.73	5.38	1.29	2.31	1.18	1.13	1.28
3	37.46	10.07	36.73	8.87	1.07	2.74	1.20	0.98	1.22
4	36.82	11.78	38.00	6.36	1.00	2.65	1.52	1.03	1.20
5	36.50	11.02	36.32	8.97	1.36	2.53	0.87	0.99	1.24

The radiochemical property results of the gamma spectrometry investigation are shown in Table II.

TABLE II

Radioactivity/(Bq kg^{-1}) of nuclides in blast furnace slag

Sample number	^{226}Ra	^{228}Ra	^{40}K
1	212	42	410
2	191	42	372
3	151	29	306
4	163	33	335
5	191	33	336

The slag phase composition, investigated by the x-ray diffraction method, is shown in Table III.

In anion exchange ion chromatography investigations, the column and the precolumn were filled with different initial concentrations of phthalic acid (1.5 mM, 2.0 mM, 2.5 mM and 3.0 mM) and 5% (V/V) acetonitrile as eluent, with pH correction from 3 to 5. Calibration by standard addition and calibration with external standards were applied. Optimization of the chromatography system resulted in a flow-rate of 1.5 mL/min, with a 20 bar pressure (valid for the column alone)

TABLE III

Slag phase composition

Phase	Sample				
	1	2	3	4	5
glassy	+	+	+	+	+
$Ca_3Si_2O_7$	+	+	+	+	+
$\alpha Ca_3Si_2O_7$	+	+	+	+	+
$\gamma 2CaOxSi_2O_2$	+	+	+	+	+
$\beta 2CaOxSiO_2$	+	+	+	+	+
$\alpha 2CaOxSiO_2$	–	+	+	–	+
$CaOxFe_2O_3$					
$CaOx2Fe_2O_3$ mixture	+	–	+	+	+
$2CaOxFe_2O_3$					
$2FeOxSiO_2$	+	+	+	+	+
$CaMg_3 (SiO_4)_3$	–	–	+	–	–
$CaOxMgOxSiO_2$	–	+	+	+	+
$2MgOxAL_2O_3x5SiO_2$	–	–	+	+	+
$CaSi_2O_5xH_2O$	+	–	–	+	–
$NaAlSi_3O_8$	–	–	+	–	–
$Ca_4Si_3O_9(OH)_2$	+	+	–	–	–
$Ca_2Al_2SiO_7$	–	–	–	+	+

TABLE IV

Ion chromatography analysis of anions (mass fractions/ppm) in the system: slag-eluent

Sample number	time of contact (hours)	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}
1	1	3.7948	4.8000	4.5190	8.9807	9.2466	9.7227
	24	2.4825	4.7811	4.4939	8.8202	8.6987	9.2242
	72	1.5214	4.8102	4.5392	8.6356	8.8056	9.4258
	504	–	4.8777	4.7048	8.2888	8.9947	9.5700
	720	–	4.7055	4.5197	7.9221	8.1171	10.9831
2	1	3.5005	4.1368	3.9429	9.9810	8.3735	10.1787
	24	2.5289	4.1299	3.0076	9.9732	9.7753	10.5897
	72	2.0371	4.7288	3.0845	9.8664	8.0555	9.6292
	504	–	4.3916	3.9574	9.4351	9.2949	10.5245
	720	–	4.0348	3.9584	9.1854	9.9750	10.0131
3	1	3.7801	4.8510	3.8891	9.9262	7.8220	11.5525
	24	2.7630	4.3513	3.8581	9.9376	7.8528	11.2841
	72	1.7199	4.3195	3.9362	9.8325	8.1385	11.6596
	504	–	4.3300	3.2078	9.8899	7.2732	12.8253
	720	–	4.2372	3.1854	8.7481	6.9304	13.2444
4	1	3.7010	4.3785	4.7065	9.8109	9.9780	10.5001
	24	2.9110	4.4801	4.7101	9.7219	9.9710	11.1226
	72	1.0440	4.4800	4.6988	9.7116	9.1990	12.0354
	504	–	4.4655	4.7111	9.6993	8.9634	12.0911
	720	–	4.4299	4.6999	9.7001	8.9115	12.0905
5	1	3.7814	4.4895	4.7669	9.8940	9.9765	10.8756
	24	2.2205	4.4780	4.6991	9.9100	9.8944	11.0136
	72	1.0091	4.4712	4.6891	9.8130	9.9732	12.2001
	504	–	4.4654	4.6790	9.7950	9.9699	13.0001
	720	–	4.4399	4.6990	9.8910	9.8455	13.1003
standard eluent (c_0)		4.9853	4.8961	4.7676	9.9840	10.2972	10.2872
elution time/min		1.567	2.177	2.647	3.152	3.735	5.865

and a total retention time of 13 min, which enabled elution of the system peak. The injector volume was 100 μL. The full scale was 5 μS cm^{-1}.

In order to test ion-exchange properties of the slag, a 1g sample of slag was taken (dried at a temperature of 105 °C) and put in contact with 10 mL of distilled water, then in 10 mL of tap water and with 10 mL of eluents with 5 ppm of fluoride, chloride and nitrite each, and 10 ppm of bromide, nitrate and sulphate each (Table IV).

The anion concentration changes were observed in periods of 1 to 720 hours at 20 °C. Sample solutions must always be filtered through a 0.45 μm membrane filter.

Sample with the anion concentration higher than 10 mg/l were diluted prior to anion determination because of high concentrations of other salts present in the medium to avoid column saturation effect.[21]

After injection of the sample, ions were detected following elution from the column. First, the fluoride ion was eluted after 1.567 min and the last to elute was the sulphate ion after 5.865 min (Table IV). An additional benefit of this method is the possibility of simultaneous determination of fluoride, chloride, bromide, nitrite, nitrate and sulphate during the same analytical run.

RESULTS AND DISCUSSION

The blast furnace slag is a material that requires special investigation. Chemical analyses, used for observing the slag characteristics during a period of five months, show a well-balanced chemical composition (Table I), defined by the ratio of acid and basic components:

$$\frac{n(CaO)}{n(SiO_2)} = 0.98 \cdot 1.13; \quad \frac{n(CaO+M_SO)}{n(SiO_2)} = 1.15 \cdot 1.28.$$

The high quality of the slag from Željezara Sisak is proved by the low values of radioactive contamination (Table II). Maximum values of radioactive contamination for materials used in civil engineering (buildings,structures) must not exceed 4×10^2 Bq kg^{-1} for ^{226}Ra; 3×10^2 Bq kg^{-1} for ^{232}Th; 5×10^3 Bq kg^{-1} for ^{40}K. The sum total of radioactive elements should be below 4×10^3 Bq kg^{-1}.[10] All the analyzed samples contain a glass phase, $Ca_3Si_2O_7$ (RANKINITE), $\alpha Ca_3Si_2O_7$ (KILHONATTE), $\gamma 2CaC \cdot SiO_2$ (SHANNONITEO), $\beta 2CaO \cdot SiO_2$ (LARNITE) and $2FeO \cdot SiO_2$ (FAYALITE) (Table III).

Accurate anion determination in complex matrices continues to be one of the most challenging areas in analytical chemistry.[22] Resin could be used not only to preconcentrate but also to separate complex matrices prior to an instrumental analysis by a conductometric analysis. Relative background conductance and detector response are predicted using different concentrations of phthalic acid. Computer simulation and experimental investigations were carried out of the behaviour of anions and six system peaks in ion exchange chromatography. The detector response was used both to qualitate (by the time the anion remains in the column) and to quantitate (by the strength of the response) the anion.

After the injection of the media, the nitrite sample (0.8 mg/L) was eluted after 3.1 min and nitrate (1.9 mg/L) after 4.4 min, using 2.5 mM of phthalic acid and 5% (V/V) acetonitrile, at a flow rate of 1.4 mL/min.

Pfaff and Brackhoff[17] report that NO_3^- elutes after 5.8 min at a flow rate of 1.5 mL/min but using a different eluent (1.4 mM sodium carbonate and 0.2 mM sodium bicarbonate). An IC anion column supersep provides sharp, symmetrical peaks, good resolution and a short time of analysis.

Determination of these ions by ion chromatography gives reproducible results over wide concentration ranges. The technique involves minimum handling and sample preparation.[18] An additional benefit is the possibility of simultaneous determination of fluoride, chloride, bromide and sulphate during the same analytical run (Table IV).[23]

Changes in the concentration during various time intervals were observed by means of simultaneous chromatographic ion analyses. The calculations that followed gave values of the distribution coefficient (K_d) as a ratio of the anion concentration in the slag and in the solution

$$K_d = \frac{C_o - C_1}{C_1} \qquad |24|$$

C_o – anion concentration in the solution at the beginning of static equilibrium slag-eluents

C_1 – anion concentration in the solution at the end of static equilibrium slag-eluents

The K_d values (Table V) show that none of the anions, except for fluorides, form compounds with the slag. On the other hand, fluorides form compounds with the slag after having been in contact with the medium for 72 hours. K_d calculations show that fluoride adsorption took place in solutions, or that fluoride anions were exchanged with slag constituents.

The negative values of K_d with SO_4^{2-} point to the possibility of sulphate component dissolution. The precise ratio of adsorption and exchange should be determined by carrying out further experiments based on X-ray slag analyses (Table III). It is possible

TABLE V

Distribution coefficient for chromatographic anion analysis in slag

Sample number	t/h	K_d					
		F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}
1	1	0.31	0.02	0.05	0.11	0.11	0.06
	24	1.01	0.02	0.06	0.13	0.18	0.11
	72	2.28	0.02	0.05	0.16	0.17	0.09
	504	4.98	0.00	0.01	0.20	0.14	0.07
	720	4.98	0.04	0.05	0.26	0.27	−0.06
2	1	0.42	0.18	0.21	0.00	0.23	0.01
	24	0.97	0.18	0.22	0.00	0.05	−0.03
	72	1.45	0.03	0.20	0.00	0.28	0.07
	504	4.98	0.11	0.20	0.06	0.11	−0.02
	720	4.98	0.21	0.20	0.09	0.03	0.03
3	1	0.32	0.01	0.22	0.00	0.32	−0.11
	24	0.80	0.12	0.23	0.00	0.31	−0.09
	72	1.90	0.13	0.21	0.01	0.26	−0.12
	504	4.98	0.13	0.49	0.01	0.41	−0.20
	720	4.98	0.15	0.50	0.14	0.48	−0.22
4	1	0.35	0.12	0.01	0.02	0.03	−0.02
	24	0.71	0.19	0.01	0.03	0.03	−0.07
	72	3.77	0.19	0.14	0.03	0.12	−0.14
	504	4.98	0.10	0.01	0.03	0.15	−0.15
	720	4.98	0.10	0.01	0.03	0.15	−0.15
5	1	0.32	0.09	0.00	0.01	0.03	−0.05
	24	1.24	0.09	0.01	0.01	0.04	−0.06
	72	3.94	0.09	0.02	0.02	0.03	−0.16
	504	4.98	0.10	0.02	0.02	0.03	−0.21
	720	4.98	0.10	0.01	0.01	0.04	−0.21

that a fluoride ion could get into the slag crystal phase. No elution of ions from the slag in redistilled or tap water was noticed.

Detailed slag characterization by ion chromatography has proved that this is a chemically inert material whose anions do not elute into the environment. On the other hand, since slag has proved to be a very good fluoride adsorbent, possibilities of slag application are extended to environmental protection in technological processes.

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SAŽETAK

Ionsko-kromatografska analiza aniona u eluatima troske

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Promatrane su interakcije F^-, Cl^-, Br^-, NO_3^-, NO_2^- i SO_4^{2-} iz troske visoke peći s otopinama aniona u trajanju od jednog sata do 30 dana.

Anioni su određivani ionsko-kromatografskom analizom, prilagođenom različitim omjerima aniona u eluatima. Rezultati elucije pokazuju inertnost sustava. Iznimka su fluoridi koji se vežu na trosku. Faktori zasićenja sustava fluoridima ekperimentalno su određeni i izračunani s pomoću koeficijenata distribucije.