ASSESSMENT OF THE CHEMICAL AND MINERALOGICAL COMPOSITION OF AIR-COOLED BLAST-FURNACE SLAG FOR ITS USE AS CONCRETE AGGREGATE

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Samples of blast-furnace slag from VSŽ (East-Slovak Metallurgical Works) Košice, of various ages and granulometry were studied with respect to their chemical and mineralogical composition. Their tendency to ferrous and γ-dicalcium silicate disintegration was assessed, as well as their hydraulic activity under normal and hydrothermal conditions. Within the time intervals followed, the experiments showed the slags to be uniform in their properties and suitable for their application as aggregate for concrete.

INTRODUCTION

Granulated blast-furnace slags have found a wide field of utilization in the manufacture of cement and cement-free binders. At present, it is deemed advisable to investigate thoroughly also the properties of air-cooled blast-furnace slag in order to promote ist utilization as concrete aggregate.

Chemical stability is one of the elementary requirements in evaluating any concrete aggregate. Dicalcium silicate, one of the components present in some slags, may be responsible for spontaneous disintegration due to polymorphous transformation of the metastable β-form into the stable γ-form, which involves an increase in volume by roughly 10%.

The chemical composition used to be the basic criterion for assessing the tendency of slags to "falling" [1–3]. Slags with a ratio of calcium oxide to silicon oxide exceeding 1.2 were regarded as liable to disintegration [3]. On the basis of this, the standard for slag aggregate [4] limited the content of the given oxides: CaO max. 43% and SiO_2 min. 30%. The foreign standard [5] stipulates the following requirements for slags to be used as concrete aggregate:

$$A : CaO + 0.8\,MgO \leq 1.2\,SiO_2 + 0.4\,Al_2O_3 + 1.75\,S$$

$$B : CaO \leq 0.9\,SiO_2 + 0.6\,Al_2O_3 + 1.75\,S$$

Apart from the requirements mentioned above, [5] stipulates that propensity towards disintegration should be tested experimentally and possibly also petrographic analyses performed.

The aim of the present contribution was to evaluate the properties of air-cooled blast-furnace slags from VSŽ Košice with respect to their chemical and mineralogical composition. The properties of the slags are assessed while taking into account factors such as the slag type, age and grain size fraction. The results have been supplemented with investigations of the properties of slag after its recrystallization brought about by annealing, and of its hydraulic properties at room temperature as well as under hydrothermal conditions.

EXPERIMENTAL

Samples of VSŽ Košice blast-furnace slag of the following two kinds were used in the investigation:

- slag aggregate aged about 3 months
- air-cooled slag roughly 10 to 15 years of age. The slag taken from the heap were ground into 0–4 mm, 4–8 mm and 8–16 mm fractions on a laboratory crusher.

For the sake of comparison with the slags mentioned above, VSŽ slag samples of different ages (1 month, 6 months, 2 years) were taken, as well as samples of finely granulated blast-furnace slag. As typical example of "falling" type slag, sample was taken from refining ferrochrome production at the Orava Ferroalloy Works Istebné.

The chemical composition of the slags, established by classical chemical analyses, is listed in Table I.

The mineralogical composition of slags was determined by X-ray phase diffraction analysis, using the Philips diffractometer (CuK_α-radiation) with the PW 1050 goniometer.

The infrared spectra (IR) were recorded with a Perkin-Elmer 983 G spectrometer using KBr pressed-disk technique. The spectra were measured in the range 2000–400 cm^{-1}, where the bands assigned to stretching and bending vibrations of Si-O groups of slags were analyzed.

The sensitivity of the slags for their "falling" was tested in accordance with procedure stipulated for this purpose by the standard for slag aggregate [4]. The propensity to ferrous disintegration was measured by long-term immersion in water, that to silicate disintegration by the autoclave test.

Sample No. 2 (Table I) was recrystallized by heating at 900°C for 24 hours.

Selected samples (mesh 0.025 mm undersizes) were used to study their hydraulic properties under normal as well as under hydrothermal conditions. Apart from aqueous suspensions of the slag alone, also suspensions of 1:1 mixtures with Portland cement and those of Portland cement alone were prepared. In all the

Table I

Chemical composition of slags used in the tests

Component	1	2	3	4	5	6	7
	Content of the component in wt.% VSŽ Košice, air-cooled						
	1mth	3mths	6mths	2yrs	10–15yrs	VSŽ gran.	OFZ Ist.
SiO_2	39.45	40.36	39.34	39.48	39.03	39.52	33.42
Al_2O_3	5.99	5.59	6.75	6.05	6.79	5.55	4.50
Fe_2O_3	0.78	1.51	1.70	1.13	0.98	0.80	1.07
CaO	39.03	37.23	37.64	38.53	38.24	39.32	44.92
MgO	9.25	8.37	8.26	9.64	9.35	9.93	11.00
S[1]	1.32	1.05	1.56	1.42	1.52	0.32	0.39
S[2]	0.44	0.33	0.45	0.48	0.50	0.43	0.12
S[3]	0.20	0.21	0.44	0.22	0.26	0.56	0.10
Na_2O	0.38	0.42	0.36	0.36	0.38	0.37	0.10
K_2O	0.80	0.76	0.92	0.78	0.78	0.79	0.04
ign.loss	1.47	3.34	2.52	1.23	1.61	1.36	3.67

[1] total sulphur as SO_3 (sum of sulphate and sulphide sulphur expressed as SO_3)
[2] sulphide sulphur (S^{II})
[3] sulphate sulphur expressed as SO_3

instances, a 10:1 ratio of water to the solids was employed. In the tests under hydrothermal conditions, the reactants in teflon crucibles were placed in stainless steel high-pressure cylinders and heated in the rotary frame of a thermostat at 190°C (saturated water vapour pressure 1.24 MPa) for a period of 24 hours.

RESULTS AND DISCUSSION

Chemical composition and disintegration of slags

The results listed in Table I show that the samples of air-cooled and those of granulated blast-furnace slag have similar contents of the main components (SiO_2, CaO). The comparison given in Table II indicates that the chemical composition of slags 1 through 5 conforms to the requirements for chemical stability according to the respective standards [4, 5].

The sample of disintegrating slag differs from the blast-furnace slags primarily by its lower SiO_2 content and its higher CaO content, and as a result of this does not meet the requirements of the standard mentioned (Table II).

The chemical stability was proved by the disintegration tests for slag aggregate: slags designated 1 through 5 in Table I have passed the autoclave test (propensity to silicate disintegration) as well as the water immersion test (propensity to ferrous disintegration). The propensity to disintegration was not measured on the granulated slags (sample 6), as it does not exist in the grain sizes required for the test.

Mineral composition of the slags

The mineral composition was assessed in relation to the type of slag, and in the case of air-cooled blast-furnace slag also in that to the age and granulometry.

The type of slag

A comparison of diffraction patterns of air-cooled, granulated and disintegrated slags is given in Fig. 1. The mineral composition of the blast-furnace slags has been significantly affected by the way they have been cooled. While the glassy phase prevails in the granulated slag, the air-cooled slag is characterized by the presence of a melilitic phase (solid solution of ackermanite and gehlenite), with a minute proportion of anhydrite and feldspars. The presence of γ - dicalcium silicate (γ-C_2S)[1], which is a prevailing component of disintegrating slags from the manufacture of refining ferrochromes (Fig. 1c), was not established.

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[1] The symbols of oxides are those used in the chemistry of cement: $C = CaO$, $M = MgO$, $S = SiO_2$, $H = H_2O$, $F = Fe_2O_3$

Table II

Assessment of the chemical composition of the slags according to BS 1047 [5]

Requirement A : $CaO + 0.8\ MgO \leq 1.2\ SiO_2 + 0.4\ Al_2O_3 + 1.75\ S$

Slag type			$CaO +$ $0.8\ MgO$	$1.2\ SiO_2 +$ $0.4\ Al_2O_3 +$ $1.75\ S$	Evaluation
1		1 mth	46.49	52.05	satisfact.
2	VSŽ	3 mths	43.93	52.50	satisfact.
3	air-	6 mths	44.25	52.64	satisfact.
4	-cooled	2 yrs	46.24	52.28	satisfact.
5		10–15 yrs	45.72	52.21	satisfact.
6	VSŽ granulated		47.26	52.49	satisfact.
7	OFZ Istebné		53.72	42.59	unsatisf.

Requirement B : $CaO \leq 0.9\ SiO_2 + 0.6\ Al_2O_3 + 1.75\ S$

Slag type			CaO	$0.9\ SiO_2 +$ $0.6\ Al_2O_3 +$ $1.75\ S$	Evaluation
1		1 mth	39.09	41.41	satisfact.
2	VSŽ	3 mths	37.23	41.51	satisvact.
3	air-	6 mths	37.64	42.11	satisfact.
4	-cooled	2 yrs	38.53	41.65	satisfact.
5		10–15 yrs	38.24	41.86	satisfact.
6	VSŽ granulated		39.32	41.75	satisfact.
7	OFZ Istebné		44.92	33.46	unsatisf.

Similar results were obtained in the assessment of mineral composition by IR spectroscopy (Fig. 2). Characteristic vibrations of ackermanite [6] overlapping the vibrations of the other, less represented component of the melilitic phase, gehlenite [7] were detected in the spectrum of air-cooled slag (Fig. 2a). The stretching vibrations of Si-O groups in the diortho-group of Si_2O_7 absorb in the range 1200–750 cm^{-1}. In the region 800–400 cm^{-1} the stretching vibrations of Mg-O in the MgO_4 tetrahedra (640–580 cm^{-1}) overlap the bending vibrations of Si-O groups [6]. The wide absorption bands of stretching (1022 cm^{-1}) and bending (674, 490 cm^{-1}) vibrations of Si-O groups, observed in the spectrum of the granulated slag (Fig. 2b), are characteristic for the vitreous amorphous phase [6, 8]. The band at 876 cm^{-1}, similarly to that at 875 cm^{-1} in Fig. 2a, is attributed to bending vibrations in the CO_3 group. The absorption bands in the spectrum of the disintegrating slag belong to Si-O vibrations in γ-C_2S [9].

Age of slag

According to diffraction patterns, air-cooled slag of various age was found to be melilitic, with a small portion of feldspars. These were compared with the diffractions (their position and intensity) of pure powdered standards (ackermanite and gehlenite). From the difference Δ (distance in mm) of two significant diffraction maxima in the range of angles 8–9 Θ (the average of two series of numerous measurements) it was possible to estimate (corroborated also by the results of chemical analysis) the C_2MS_2 : C_2AS ratio, which turned out to be nearly 75 wt.% : 25 wt.% as seen in Fig. 3.

Grain size fraction of the slag

The results of IR nad X-ray analyses of the individual separated granulometric fractions revealed no significant differences in their mineral composition,

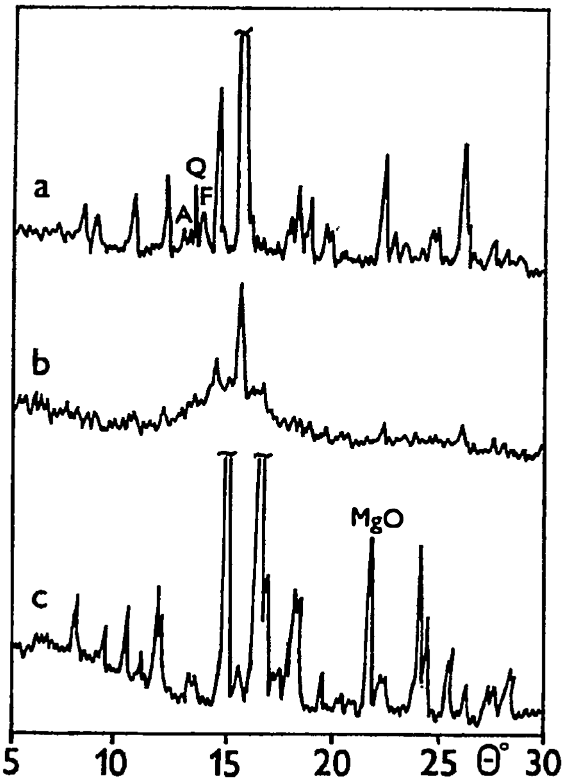

Fig. 1. X-ray diffraction patterns of the slags: a) blast-furnace air-cooled slag, age 3 months (symbols: A–anhydrite, Q–quartz, F–feldspar, non-marked diffractions – melilitic phase), b) blast-furnace granulated slag, c) slag from refining ferrochrome production – disintegrating (non-marked diffractions – γ-C_2S).

except for a mild increase of silica content in the fine fractions compared with the average composition.

Slag recrystallization

IR spectra of slag No.2 (Table I) in its original and after recrystallization are shown in Fig. 4. An increase of absorption bands intensities at 937, 852, 641 and 589 cm^{-1}, which are typical for ackermanite [6], indicates the recrystallization resulted in a higher content of crystalline phase. At the same type, the bands corresponding to stretching (1481 and 1431 cm^{-1}) and bending (875 cm^{-1}) vibrations of CO_3 group disappear.

Hydration of slag

Products of hydration under normal conditions

Because hydration under normal conditions resulted in only minute diffuse diffractions in X-ray diffraction patterns, preference was given to studying the phase composition of hydration products by IR spectroscopy. The pattern of absorption of the slags was found to change already after 3 months of hydration (Fig. 5a). The band of Si-O stretching vibrations at 1015 cm^{-1} disappears and the band at 985 cm^{-1} acquires the highest intensity. The Si-O vibrations of melilitic phase, which remains to be the dominant component of the slag, as well as stretching vibrations of Si-O groups in hydration products of calcium silicate hydrate type, contribute to the intensive broad band near 980 cm^{-1} [11].

In the course of hydration, also the polymorphous modifications of $CaCO_3$ are transformed. Vaterite, identified in the original slag according to the doublet at 1481 and 1413 cm^{-1} is converted to calcite with stretching vibration of CO_3 groups at 1430 cm^{-1} (Figs. 5b–d). The bending vibrations of CO_3 groups (835 and 715 cm^{-1}), similarly to the band at 1430 cm^{-1}, increase in intensity with the time of hydration.

Products of hydration under hydrothermal conditions

Compared to the slag hydrating under normal conditions (room temperature, in water), the hydrothermal conditions bring about more extensive recrystallization of the partially vitreous component of the

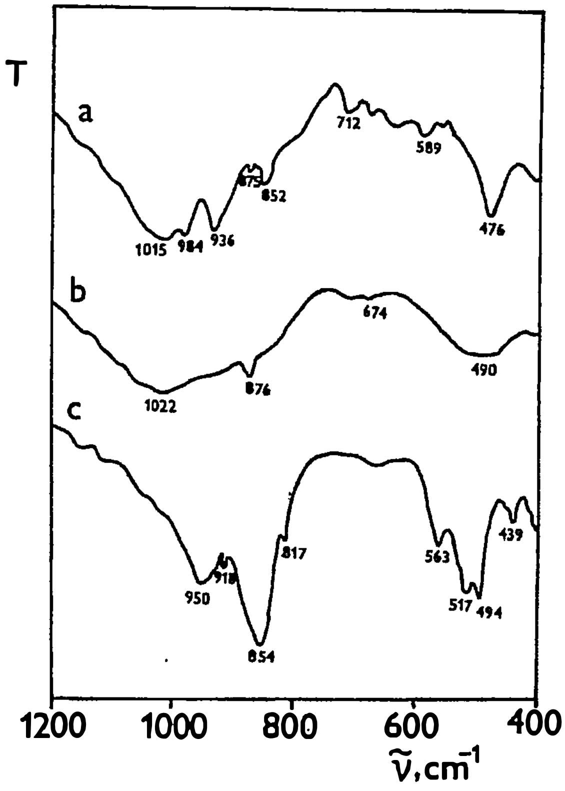

Fig. 2. IR spectra of the slags: a) blast-furnace air-cooled slag, age 3 months, b) blast-furnace granulated slag, c) slag from ferrochrome production – disintegrating.

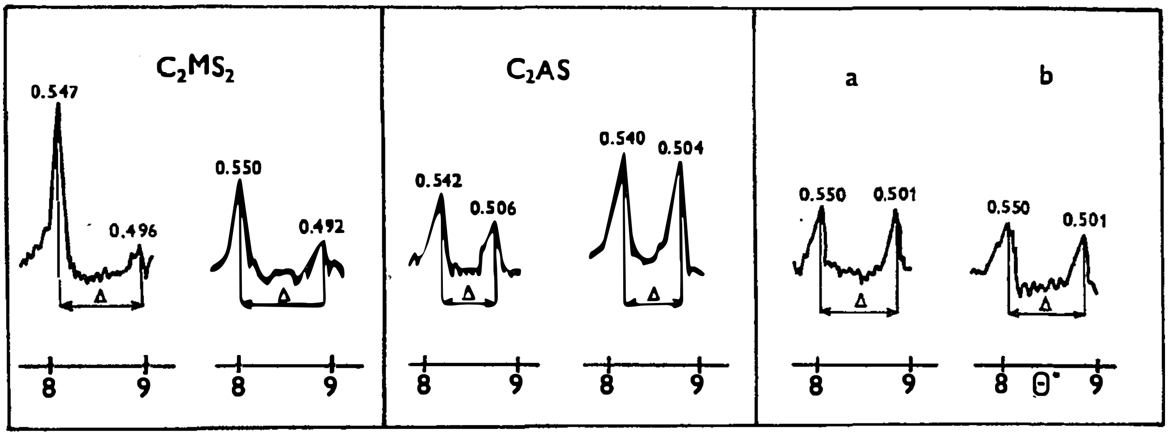

Fig. 3. Comparison of selected diffractions of pure components C_2MS_2 and C_2AS with those of air-cooled blast-furnace slag aged a) 3 months, b) 10–15 years.

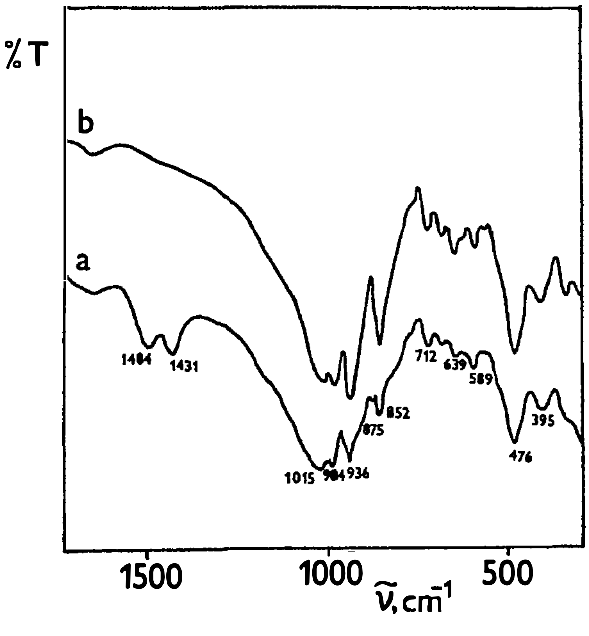

Fig. 4. IR spectra of air-cooled slag, 3 months-old: a) original sample, b) after recrystallization.

melilitic phase. Fig. 6 shows diffraction patterns of an aqueous suspension of slag, of a 1 : 1 slag – Portland cement mixture and of a suspension of Portland cement alone.

The X-ray diffraction pattern of powdered compact slag following hydrothermal treatment shows mainly more intensive diffractions of the melilitic phase. Compared to the original slag, one can observe only minute changes in the low angle Θ region, because the hydration. and the interactions of slag minerals create cryptocrystalline products in the system CaO-MgO-SiO_2-Al_2O_3-H_2O (CMSAH), and/or C(A,F)H_x.

Significant changes can already be observed on the pattern of products obtained by hydrothermal treatment of the 1 : 1 mixture of powdered slag with Portland cement. The interaction of the reactants brought about a distinct decrease of the content of melilitic minerals and formation of basic calcium silicates, primarily $C_2SH(A)$ and Roy's phase (from the Portland cement). A certain proportion of non-specific phases of non-stoichiometric composition in the system CaO-MgO-SiO_2-Al_2O_3 was also detected, particularly in the low Θ angle region. A share of $Ca(OH)_2$ is leftffi behind by the Portland cement.

Under the given conditions, the hydrothermal treatment of the Portland cement suspension produced for the most part dicalcium silicate hydrate $C_2SH(A)$, a minor proportion of tricalcium silicate hydrate C_3SH_2 as well as Roy's phases. There was also a substantial proportion of $Ca(OH)_2$, produced by hydration of clinker minerals C_3S and C_2S, as well as a minute non-reacted residue of these minerals.

CONCLUSIONS

The results of laboratory tests, aimed at assessing the chemical and mineralogical composition of air-cooled blast-furnace slag from VSŽ Košice, can be summarized as follows:

- as regards the chemical compositon of the slag, the samples meet the requirements of the respective standards and regulations. The slags were not found to be the type showing propensity to falling;
- the air-cooled slags are melilitic, with a minute portion of anhydrite and feldspars. No significant

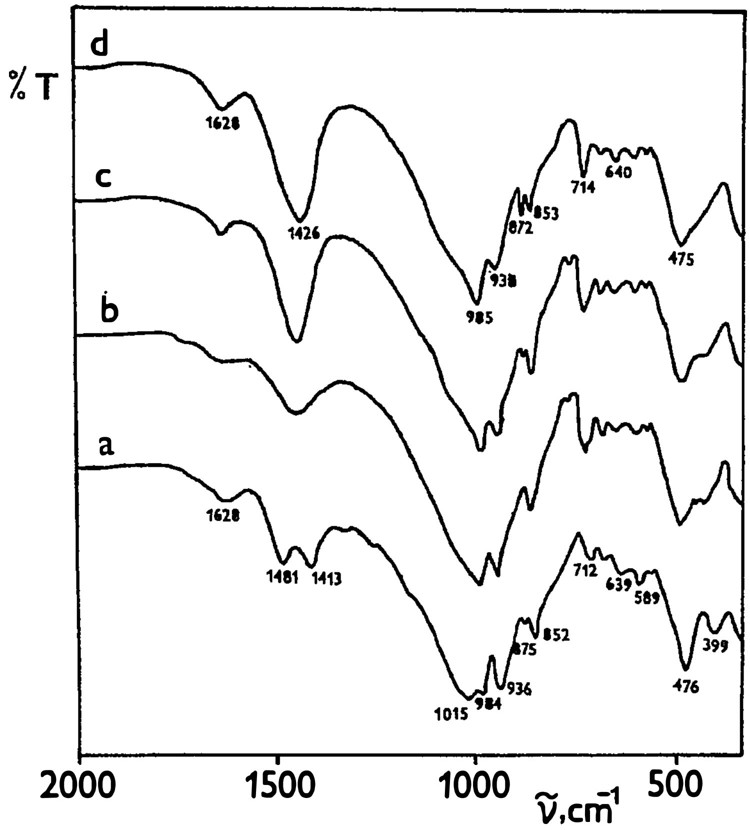

Fig. 5. IR spectra of the slag: a) original air-cooled blast-furnace slag, b) suspension in water after 3 months of standing, c) suspension in water after 6 months of standing, d) suspension in water after 1 year of standing.

difference between the various samples relating to their age and grain size was established;

- under normal conditions of hydration, powdered slag alone produces minor amount of hydration products of CSH type. Under hydrothermal conditions, the melilitic phase recrystallizes, producing minute amounts of cryptocrystalline phases in the system CaO-MgO-SiO_2-Al_2O_3-H_2O;
- from the standpoint of both chemical and mineralogical composition, the slag is suitable for use as aggregate for concrete.

References

[1] Gutt W., Russell A.D.: J. Mater. Sci. *12*, 1869 (1977).
[2] Matoušek M.: Stavivo *30*, 103 (1952).
[3] Stork J.: *Technológia betónu I*, vyd. SAV Bratislava 1954, p. 31.
[4] ON 72 20 40 Struskové hutné kamenivo do betónu.
[5] BS 1047: British Standard Specification for Air-cooled Blast-furnace Slag Aggregate for Use in Construction. BSI (1983).
[6] Kolesova V.A., Ismatov A.A., Toropov N.A.: Izv. Akad. Nauk. SSSR, Neorg. Mater. *5*, 1594 (1969).
[7] Kolesova V.A., Ismatov A.A.: Izv. Akad. Nauk. SSSR, Neorg. Mater. *7*, 1279 (1971).
[8] Dowty E.: Phys. Chem. Minerals *14*, 122 (1987).
[9] Bensted J., Prakash Varma S.: Cem. Technology *5*, 256 (1974).
[10] Ghost S.N., Handoo S.K.: Cem. Concr. Res. *10*, 771 (1980).

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POSÚDENIE CHEMICKÉHO A MINERÁLNEHO ZLOŽENIA VZDUCHOM CHLADENEJ VYSOKOPECNEJ TROSKY PRE JEJ POUŽITIE AKO KAMENIVA DO BETÓNU

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Vzorky vysokopecnej trosky z VSŽ Košice boli študované z hľadiska ich náchylnosti k rozpadavosti, ktorá by mohla obmedziť ich využitie ako hutného kameniva do betónu.

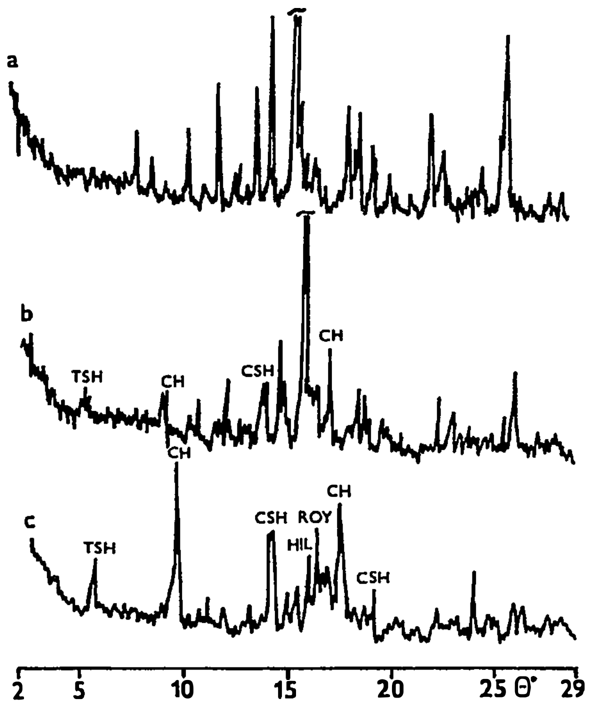

Fig. 6. X-ray diffraction patterns of aqueous suspensions under hydrothermal conditions: a) air-cooled blast-furnace slag (diffractions are those of melilite and a minute amount of merwinite and/or monticellite), b) a mixture of blast-furnace slag and Portland cement, c) Portland cement alone (CH=$Ca(OH)_2$, CSH=$C_2SH(A)$, ROY=Roy's phases, TS=C_3SH_2, HIL=$C_2SH(B)$).

Po stránke chemického zloženia vzduchom chladené vysokopecné trosky vyhovujú požiadavkam príslušných noriem a predpisov na chemickú stálosť. Z hľadiska minerálneho zloženia sú vzduchom chladené trosky melilitické, s nepatrným podielom anhydritu a živcov. Neboli zistené výraznejšie rozdiely medzi posudzovanými troskami z hľadiska ich rôzneho veku a frakcie.

Výsledky boli doplnené o sledovanie vlastností trosky pri rekryštalizácii žíhaním, ako aj jej hydraulických vlastností pri normálnej teplote a za hydrotermálnych podmienok. V porovnaní s troskou hydratujúcou pri normálnych podmienkach prejavila sa za hydrotermálnych podmienok výraznejšie rekryštalizácia čiastočne sklovitého podielu melilitickej fázy trosky za vzniku nepatrného množstva kryptokryštalických produktov. Výsledky skúšok preukázali rovnomernosť vlastností trosiek a potvrdili ich vhodnosť pre použitie ako hutného kameniva do betónu.

Obr. 1. Röntgenové difrakčné záznamy trosiek: a) vysokopecná vzduchom chladená – vek 3 mesiace – (symboly: A–anhydrit, Q–quartz, F–feldspar, neozn. difrakcie – melilitická fáza), b) vysokopecná granulovaná, c) z výroby rafinačných ferochrómov – rozpadavá – (neozn. difrakcie – γ-C_2S).

Obr. 2. IČ spektrá trosiek a) vysokopecná vzduchom chladená, – vek 3 mesiace – b) vysokopecná granulovaná, c) z výroby rafinačných ferochrómov – rozpadavá.

Obr. 3. Porovnanie vybraných difrakcií čistých zložiek C_2MS_2 a C_2AS s difrakciami vysokopecnej vzduchom chladenej trosky s vekom 3 mesiace (a) a 10–15 rokov (b).

Obr. 4. IČ spektrá vzduchom chladenej trosky s vekom 3 mesiace: a) pôvodná vzorka, b) po rekryštalizácii.

Obr. 5. IČ spektrá pôvodnej vysokopecnej vzduchom chladenej trosky (a) a suspenzií vo vode po dobu 3 mesiacov (b), 6 mesiacov (c) a 1 roka (d).

Obr. 6. Röntgenové difrakčné záznamy vysokopecnej vzduchom chladenej trosky (a) (difrakcie prislúchajú melilitom a nepatrnému podielu merwinitu, resp monticellitu, suspenzie trosky a cementu (b) a suspenzie zo samotného cementu (c) za hydrotermálnych podmienok; CH = $Ca(OH)_2$, CSH = $C_2SH(A)$, ROY = Royové fázy, TSH = C_3SH_2, HIL = $C_2SH(B)$.