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Properties of concrete pavements prepared with ferrochromium slag as concrete aggregate

J. Zelić

Faculty of Chemical Technology, Department of Inorganic Technology and Metallurgy, Teslina 10/5, HR-21000 Split, Croatia

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Abstract

This paper presents the results of investigation related to both the properties of the ferrochromium slag and the standard physical and mechanical properties of Portland cement concrete pavements (PCCP) made with this slag as aggregate, according to the relevant Croatian standards. Slag is formed as a liquid at 1700 °C in the manufacture of the high-carbon ferrochromium metal and, by slow cooling in the air, the slag crystallizes to give a stable $CaO-MgO-Al_2O_3$–silicate product with mechanical properties similar to basalt. With a proper selection of slag as an artificial aggregate, concrete pavements with compressive strengths, wear resistance and specific weight higher than in those from natural (limestone) aggregate in commercial Portland cement, type CEM II/B-S 42.5 (EN 197), can be made. The 28-day compressive strength of the concretes made with original unfractioned slag and with standard limestone as aggregates (w/c=0.64 and 350 kg/m^3) reached the values of 57.00 MPa and 36.70 MPa, respectively. Volume stability, high volume mass, good abrasion resistance to wear and crushability make this reinforced slag concrete suitable for wearing courses of concrete pavements for traffic load classes 1 and 2 where carbonate stone material (limestone) mainly does not meet the Standard Technical Requirements for cement concrete slab pavements according to the relevant Croatian standard.

Keywords: Ferrochromium slag; Characterization; Mechanical properties; Aggregate; Concrete

1. Introduction

According to the Technical Requirements for the construction of wearing courses in highway pavement for traffic load classes 1 and 2 (relevant Croatian standards), the wearing courses of either bitumen (asphalt) or concrete pavements must be based on materials of igneous origin. If, in the wide region of Dalmatia, Croatia, there is no source of such materials, the crushed rock aggregates of the basalt type for wearing courses have to be transported from more distant locations. Due to very high prices of these stone materials, the research for more economic solutions than the standard ones is called for.

The best-known and quantitatively most important slag is the blast furnace slag, which has been widely used in cement and concrete technology as a cementing material or as an aggregate [1].

In recent year, the potential use of the ferrochromium slag both as addition to cement clinker in the process of grinding and as an aggregate in concrete or asphalt mixes has been investigated [2,3]. Kuznetsova et al. [2] have investigated the effect of various methods and conditions of granulation on the process of hardening of binding materials based on Portland cement clinker and slag from the low-carbon ferrochromium production.

The high-carbon ferrochromium slag is waste material obtained in the manufacture of high-carbon ferrochromium, FeCr(C). The high-carbon FeCr metal with 65% Cr (min) content is produced in electro-arc furnaces by the carbothermal process out of the oxide of chromium ore (the chrome spinel with the Cr_2O_3-to-FeO ratio more than 2.5) with coke as the reducing agent at the temperature of about 1700 °C. Both the liquids of the FeCr metal and of the slag flow out into ladles. After stratification of the metal from the slag by means of their different specific gravities, the molten slag, slowly cooling in the air, forms a stable crystalline

E-mail address: jelica.zelic@st.hinet.hr.

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dense rock product with mechanical properties similar to basalt. This slag has been used for a long time as road construction material [3].

In the Dalmacija Ferroalloys Work, the only plant of its type in Croatia, the FeCr slag is produced in a quantity of 60,000 tons/year. Slag is composed essentially of silica, alumina, magnesia and lime with a small amount of residual ferrochromium metal. Due to economical contribution, the residual FeCr metal is removed from the original crushed (0–16 mm) slag by the "jig" treatment and delivered to the market. The slag that remains after the "jig" treatment is dumped at landfills and its accumulations represent a huge ecological problem.

The research into the possibility of application of the high-carbon ferrochromium slag from the Dalmacija Ferroalloys Works as an alternative aggregate in road construction began in 1986. A study on the use of the ferrochromium slag in asphalt mixes [4] has shown that, by combining a mixture of ferrochromium slag with stone materials of carbonate composition, satisfactory physical and mechanical properties could be obtained for application in wearing courses.

This article reports practical experiences in the study of properties of slag from the high-carbon ferrochromium production when it is used as an artificial aggregate for preparation of concrete pavements in accordance with the Croatian standards [5–7]. The overall experimental program consisted of three stages: (1) a comprehensive study of the properties of ferrochromium slag; (2) a study of the standard physical and mechanical properties of concrete pavements made with ferrochromium slag as an artificial concrete aggregate; and (3) the leaching behavior of ferrochromium slag used (a work in progress). This paper presents the results of stages (1) and (2) of the study.

As these studies aim to prove the applicability of the FeCr slag as a concrete aggregate, the slag properties were examined according to the Croatian standards for crushed aggregates [5,6]. The analysis and discussion of all the results includes a short overview of possible advantages or faults of slag used in comparison with the standard crushed limestone used as the concrete aggregate in the region of Dalmatia. All the examinations were carried out in accordance with the Croatian standards that are in the process of harmonization with ISO standards (International Standard Organization).

2. Experimental program

2.1. Materials and concrete preparation

2.1.1. Industrial blended Portland cement

Industrial blended Portland cement, produced by grinding Portland clinker and mixing with up to 5 mass% gypsum and about 30 mass% of the blast furnace slag (type CEM II/B-S 42.5 according to EN 197) in the Croatian Cement Works (the RMC Dalmacijacement, a company of the RMC Group, Kaštel Sućurac, Croatia) was used in this study.

2.1.2. Ferrochromium slag

Ferrochromium slag remains as a waste product in the production of high-carbon ferrochromium metal in the Dalmacija Ferroalloys Works, Dugi Rat, Croatia.

After crushing of the air-cooled slag to the grain size in the range of 0–16 mm (first by a hammer crusher and then by a cone beaker), the metallic globules of ferrochromium metal were removed from the crushed slag by the Remer jig treatment (Umitec Wemco Europe, Paris, France). This method is based on the stratification of grains in the water flow by means of different specific gravities: heavy grains will fall to the bottom and water will carry lighter grains to the surface. The specific gravity of slag and FeCr metal is 3.2 g/cm^3 and 7.1 g/cm^3, respectively. By the jigging action of the water flux up-and-down through a bed of the original crushed slag (rich in the FeCr metal), the following fractions were derived: (a) the FeCr metal concentrate (0–4 mm) with the 40% Cr content, (b) the FeCr metal (4–16 mm) with the 61% Cr content and (c) the slag (0–16 mm) up to the 11% Cr content.

The Dalmacija Ferroalloys Works used to produce each month about 5500 tons of original slag rich in the FeCr metal, out of which the "jig" treatment separated about 400 tons of FeCr metal (4–16 mm), about 150 tons of FeCr metal concentrate (0–4 mm) and about 5000 tons of slag (0–16 mm), which was used in the concreting experiments. A representative slag sample for our examinations was prepared by homogenization (mixing) of 12 samples of slag (Fig. 1) produced in the "jig" process during a period of 6 months.

In order to evaluate the properties of slag as concrete aggregate, an investigation has been made to fully characterize the slag after the jig treatment. The usual physical–chemical methods such as: chemical analysis, mineralogical analysis by X-ray diffraction analysis (X-ray diffractionmeter Philips PW 1010, Einhoven, Netherlands, with CuKα

Fig. 1. A photograph of the ferrochromium slag used (the grain size in the range of 0–16 mm).

radiation in the ranges of the Bragg's angles 2Θ=15–50°), thermal analyses DTA/TG (Derivatograph-MOM, Budapest, Hungary) and thermoplastic analysis by the heating microscope (Mettler Instruments TA 2000, Switzerland) were used. The petrographical properties of slag were established in the Institute for Mineralogy, Petrology and Economic Geology of Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Croatia. Thin sections of slag specimens were examined under a petrographic microscope according to HRN.B.B8.004 [8]. The analysis of the radioactivity of the ferrochromium slag was performed in the Institute for Medical Research and Occupational Health, Zagreb, Croatia. A Canberra gamma-spectrometer (Canberra Ind., CT, U.S.A.) with a Ge(Li) detector by coupling with a 4096 multi-channel analyzer (resolution of 80 to 1500 keV) was used.

The slag was tested for the volume mass, granulometry and compressive strength, abrasion and wear resistance, frost resistance, water absorption, alkali-silica reaction and crushing value in accordance with the Croatian standards [5,6]. The slag samples for the compressive strength test were preparing by sawing a slag sample to the dimensions of 70 × 70 × 70 mm by a diamond saw in dry conditions [5]. Due to rough edges and voids in the samples, the slag broke down under the saw, so that the samples were tested on irregularly shaped bodies within the framework of requirements indicated.

The test method for possible alkali reactivity of slag [9] was based on the reaction between the dissolved silica (Sc in mmol/L) and the reduction in alkalinity (Rc in mmol/L) when crushed slag was immersed in a NaOH solution at 80 °C for 24 h. The solution was filtered and analyzed for the dissolved silica content (Sc) by gravimetric methods and for the reduction in alkalinity (Rc) by titration with HCl using a phenolphthalein indicator. The results of analyses were plotted onto the Sc–Rc graph. The expansion test was determined according to the Croatian standard [10] on the mortar bars, whose size was 25 × 25 × 285 mm. A cement-to-aggregate mortar combination with one part industrial cement (CEM II/B-S 42.5) and with 2.25 part of the graded slag aggregate up to 4.00 mm in size was prepared. Mortar samples were cured for 24 h in moist air at 20 ± 1 °C and then kept in a sealed container at a temperature of 38 ± 1 °C and relative humidity of 95% for a 6-month period. Their elongation was first measured after 24 h. Successive measurements were taken after 14, 30, 60, 90, 120 and 180 days. The autoclave expansions test [11] was carried out on mortar prisms, 40 × 40 × 160 mm, that were made with the neat cement-to-slag ratio value of 2. The mortars were cured for 24 h in a humid environment (20 °C, 90% relative humidity) and their length measured on a suitable comparator. Then they were placed in an autoclave (210 N/cm^2, 216 °C) for 3 h. After cooling, their length was measured again. The expansion of mortars was defined by the changes in sample lengths before and after the autoclave process. The resistance to frost test of the slag aggregate was determined by the reference method [12], by use of the saturated Na-sulfate solution. The samples were subjected to 5 cycles of the Na-sulfate solution and subsequently dried at temperature of 100–110 °C. The loss of mass after 5 cycles was measured.

2.1.3. Crushed limestone aggregate

Crushed limestone aggregate is a commercially available limestone (The Srijane Quarry, Dalmatia, Croatia) that is usually used as a standard aggregate in concrete or in asphalt mixtures. Limestone is a natural stone material composed of 97.32 mass% calcium carbonate. The control, reference concrete was prepared by using crushed limestone aggregates divided into fractions of the particle size-to-mass% ratio as follows: (0/4 mm):(4/8 mm):(8/16 mm)=52:18:30 according to the Croatian standard [13].

2.1.4. The commercial air-entraining agent

The commercial air-entraining agent (Monolit, KGK-Karlovac, Croatia) was used.

2.1.5. Concrete mixtures

Two series of concrete mixtures were prepared. The first series of five concrete types with the water-to-cement (w/c) ratio of 0.64 and cement content of 350 kg/m^3 were made as follows:

- With unfractioned slag (particle size of 0–16 mm), marked A
- By combining the unfractioned slag (0–16 mm) with fine crushed limestone aggregate (0–4 mm), marked B
- With the concrete mixture B with the addition of 0.525 kg/m^3 of the air-entraining agent, AEA, marked C,
- With fractioned slag of particle sizes-to-mass% ratio: (0–4 mm):(4–8 mm):(8–16 mm)=52:18:30, marked D, and
- With fractioned crushed limestone with particle sizes-to-mass% ratio: (0–4 mm):(4–8 mm):(8–16 mm)=52:18:30, marked E.

Table 1 shows the mix proportions of concretes marked A–E. The absolute volume method was used in the

Table 1
The mix proportions of concretes marked A–E

Constituents, kg/m^3	A	B	C	D	E
Cement	350	350	350	350	350
Aggregate	–	–	–	–	–
Slag (0/16 mm): (0/4:4/8:8/16=24:28:47)	2107	1475	1401	–	–
Slag (0/4:4/8:8/16=52:18:30)	–	–	–	2107	–
Crushed limestone (0/4 mm)	–	517	493	–	–
Limestone (0/4:4/8:8/16=52:18:30)	–	–	–	–	1882
Water	224	224	224	224	224
Water-to-cement ratio, w/c	0.64	0.64	0.64	0.64	0.64
Air content, %	1.50	1.50	4.50	1.50	1.50
Air-entraining agent, AEA	–	–	0.525	–	–
Unit weight, kg/m^3	2681	2566	2558	2681	2456

calculation of the concrete mixture [14]. The specific gravities (in g/cm^3) of the Portland cement, ferrochromium slag and limestone used were 3.18, 3.30 and 2.70, respectively. The cement dosage in the five concrete mixtures (marked A–E) was accepted as constant at 350 kg/m^3 because this dosage is the most common in application. Concrete prepared with crushed limestone aggregate (marked E) has been used as the referent, standard sample with the Concrete Brand value of 35, MB-35. Compressive strength development tests were carried out on the concrete specimens (marked A-E) at ages of 3, 7 and 28 days. The second series of concrete mixtures (with the same composition as concrete mixes marked D and E but designed with a large cement content of 450 kg/m^3 and the water-to-cement ratio of 0.5) were prepared to study the effect of slag aggregate compared with crushed natural limestone aggregate. These concrete samples were tested for compressive strength, tensile splitting strength, flexural strength, water absorption and impermeability, abrasion, wear and frost resistance, and modulus of elasticity according to relevant Croatian standards [7]. Three cubes, two cylinders and two prisms were cast from each concrete mixture. Cubes of $150 \times 150 \times 150$ mm, cylinders of 150×300 mm and prisms of $100 \times 100 \times 500$ mm were used for compressive, splitting tensile and flexural tests, respectively. Test specimens were cured for 24 h in a humid environment (at 20 ± 1 °C, 95% relative humidity) and then kept in water storage until the 28-day testing.

3. Results and discussion

3.1. Properties of high-carbon ferrochromium slag

Table 2 presents the chemical composition of the original high-carbon ferrochromium slag (rich in the FeCr metal) and the slag after the removal of residual FeCr metal process by the Remer jig treatment that has been used in our investigation. The metallic fractions of slag are given both in the oxide and metallic forms (Cr_2O_3/Cr and FeO/Fe). Table 2 indicates that the part of the Cr_2O_3 component in the slag is by 8.3 mass% smaller after the jig treatment than in the original slag before the treatment, which was the actual aim of applied process of metal concentration and its removal from the slag. The chemical analysis provides us with the possible slag composition, but cannot be used to calculate the possible mineralogical slag composition. Both metallic components such as Cr_2O_3 and FeO are assumed to be present mainly as relatively unaltered chrome spinel or as ferrochromium metal, as spinel contains both chromium and iron oxide. No chlorides were observed in the slag and the sulphur as SO_3 content of 0.50 mass% is much lower than the allowed value of 1.00 mass%, indicating that the slag does not contain harmful components that may be found in aggregates [6].

Table 2
Chemical composition of the original high-carbon ferrochromium slag (rich in the FeCr metal) and the slag after the removal of residual FeCr metal process by the Remer jig treatment

Chemical composition, mass%	Original FeCr slag	Slag after "jig" treatment
Cr_2O_3/Cr	13.50/9.24	5.20/3.55
FeO/Fe	2.60/2.02	1.00/0.78
SiO_2	33.40	34.00
Al_2O_3	15.40	16.30
MgO	33.23	41.80
CaO	2.10	1.60
Sulphur as SO_3	0.45	0.50
Chloride	–	–

Fig. 2 shows the X-ray powder diffractogram of slag used. The presence of the solid solution of forsterite, $(Mg,Fe)_2SiO_4$, in which the Mg is partially replaced by Fe, is detected. Common-spinel ($MgAl_2O_4$), chrome-spinel ($(Mg,Fe)(Cr,Al)_2O_4$) as unaltered chromium ore and also of small amounts of enstatite ($MgSiO_3$) are found. The presence of non-reacted chrome ore indicates that the slag did not reach the state of thermodynamic equilibrium, while the presence of enstatite within the slag can be explained by the effect of arrested peritectic reaction [15].

Fig. 3 presents the schematic diffractograms of the slag used related both to standard references (the X-ray Powder Data Cards) of the pure forsterite (ASTM-21-2160) and chrome-spinel (ASTM-23-1222) minerals. A strong preferred orientation on the forsterite diffraction maximum of the *hkl* reflections as follows: (020), (021), (121), (130), (131) and (200) is detected. By direct comparisons of the diffractograms, shown in Fig. 3, it can be seen that the relation of the relative intensity of the forsterite in the slag and that in the ASTM-21-2160 Card is not same, which indicates a solid forsterite solution in the slag sample. However, in view of small shifts of diffraction maximum relative to maximum of pure forsterite, it is most likely that the Fe^{2+} ion is incorporated into the olivine structure not at all, or in a very small quantity [16]. As for spinel, with its general formula AB_2O_4, we are dealing with the group of so-called chrome-spinels, the most frequent of which are chromites, $FeCr_2O_4$, and magnesium-chromites, $MgCr_2O_4$, but the diffraction maximum, as seen in Fig. 3, best correspond to a solid solution of the chrome-spinel with the composition: $Mg(Al_{1.5}Cr_{0.5})O_4$. However, its interplanar *d*-spacings do not fully correspond to *d*-spacings of the spinel phase, suggesting that the chrome-spinel has different ratios of Mg, Al and Cr components compared to the ASTM-23-1222 Card [16].

The results of a thin section of slag examined under a petrographic microscope have confirmed the X-ray diffraction findings: forsterite, spinel, chromites, enstatite crystals, unaltered chromium ore, glassy matrix and globules of metallic ferrochromium can be seen throughout the matrix. Forsterite, the predominant phase in slag, occurs as well-formed crystals up to about 400 μm in size, with the

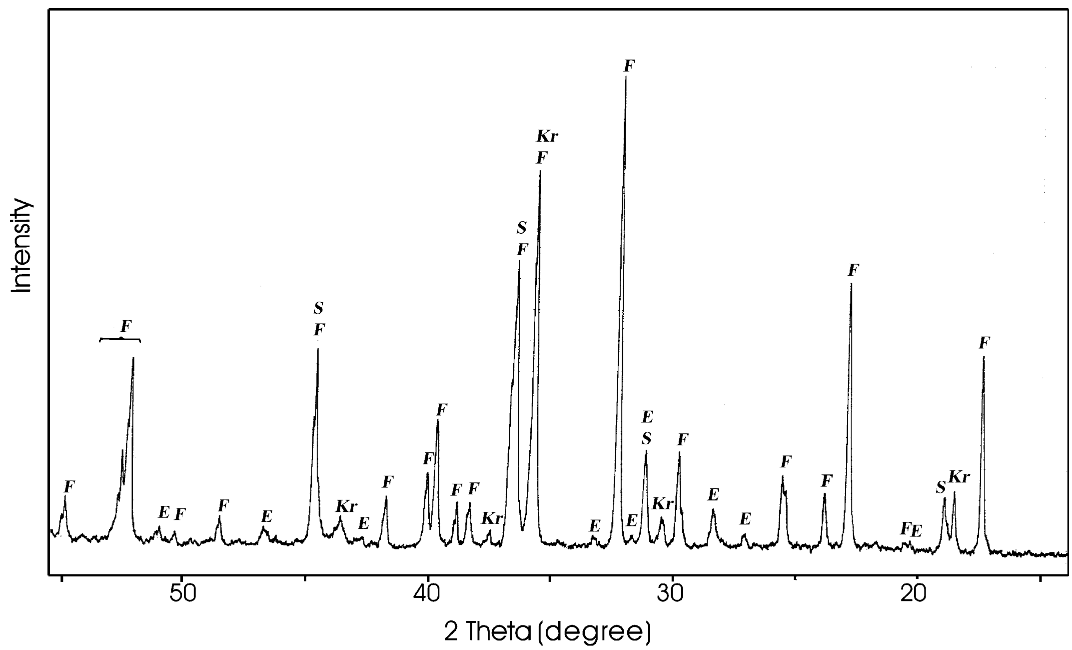

Fig. 2. X-ray powder diffractogram of the slag used. F—forsterite, $(Mg,Fe)_2SiO_4$; S—spinel, $MgAl_2O_4$; Kr—unreacted chromium-ore, $(Mg,Fe)(Cr,Al)_2O_4$; E—enstatite, $MgSiO_3$.

hexagonal habits of a high surface relief. The interference color is determined. Spinel is an isotropic mineral that occurs as triangle-like or irregular quadrilateral-like crystals up to about 150 μm in size, pinkish colored with a high surface relief. Enstatite occurs in the form of uncolored elongated crystals up to about 150–300 μm. Lath-shaped crystals of enstatite are detected through the glassy matrix between the spinel and the forsterite particles. Chromite crystals, observed in random grains, occur as isometric, oval, pseudo-transparent grains of distinctive reddish-brown

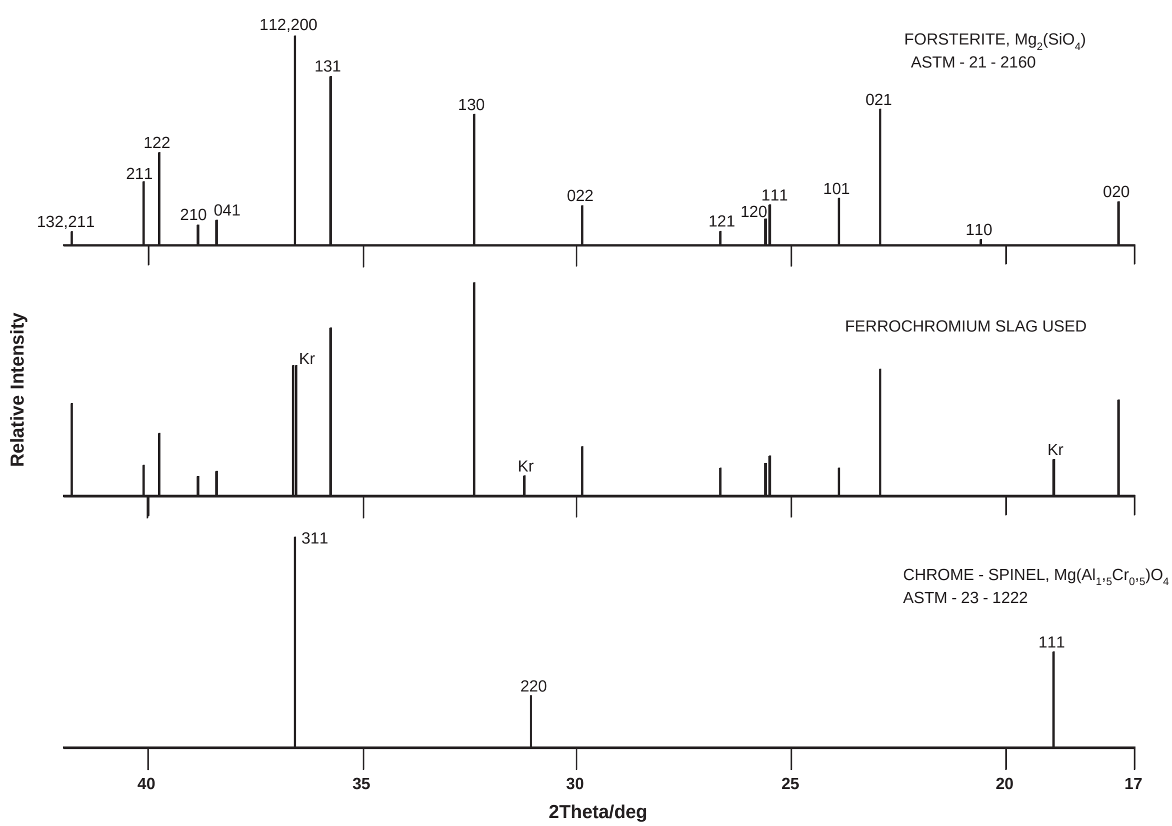

Fig. 3. Schematic diffractograms of the slag used related both to standard references of the pure forsterite and chrome-spinel minerals.

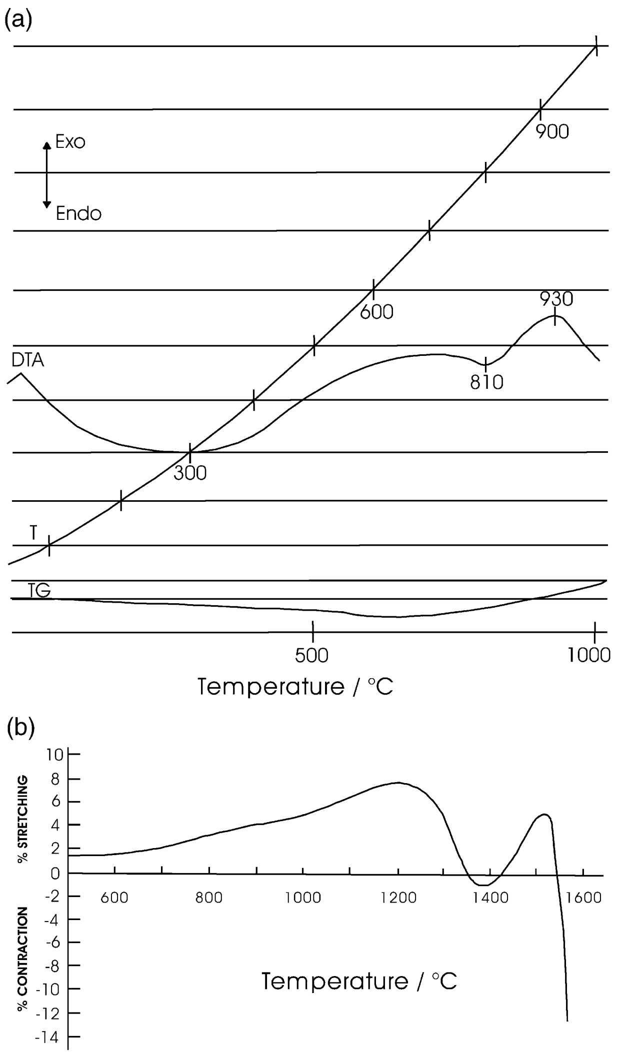

Fig. 4. (a) Thermal analysis (DTA/TG curves) and (b) thermoanalytical results of the slag used.

color. An important component, very non-uniformly distributed throughout the matrix, are the oval, non-transparent, "opaque" crystals of chromium metal that are usually surrounded by a circle of small isotropic pink crystals, most probably chrome-spinel. The glassy phase, very non-uniformly distributed, fills the irregular voids within the phases described. About 10% of the volume consists of a glassy phase. Glass is gray, somewhat clouded, with the diffraction index higher than that of the Canada balsam. The sample contains several oval bubbly voids with a diameter of 80 μm, which are unevenly spaced.

A microscopic examination of the fractured surface of slag shows that slag is dense, microscopically clearly granular, lusterless gray, very tough and hardy. Occasionally, irregular porous intrusions are observed in the dense mass, surrounded by a small layer of the chromium metal. The planes alongside which the samples were broken are brown and it is assumed to be due to the limonite substance.

Fig. 4a shows the DTA/TG measurement where both the endothermic and exothermic effects at temperature of 810 °C and 930 °C, respectively, are observed. The exothermic peak at 930 °C corresponds to the forsterite crystallization, as the additional XRD analysis of slag after thermal treatment (DTA analysis) has shown larger quantities of the forsterite phase. The relative intensity changes suggest the change in the forsterite composition [16]. An endothermic peak is observed at 810 °C, indicating the start of the slag glassy phase softening [17]. Fig. 4b shows the characteristic thermoplastic points of slag used, such as: the sintering, stretching and melting temperatures at 1370 °C, 1445 °C and of 1570 °C, respectively. Based on the results obtained, it can be concluded that a notable increase of the sample height due to stretching began at temperature of 800 °C. This is directly related to the sample mass increase as shown on the TG curve (Fig. 4a). Both the increase in height and in mass is probably the result of the process of oxidation of metals that are present in the slag. In contrast to the blast furnace slag, the slag used shows a notable contraction before the melting point in the temperature range of 1200–1400 °C (Fig. 4b). The reason of this phenomenon is not clear at present.

Table 3 presents the radionuclides together with the average of their specific activity (in Bq/kg) detected in the slag. No other radionuclides were registered. According to the State Act on the Radiation Contamination of Human Environment [18], the maximum limit of the radiation contamination in construction materials has to meet requirements according to the following expression: $(C_U/400)+(C_{Ra}/400)+(C_{Th}/300)+(C_K/5000)+(C_0/4000)\leq 1.0$, where C_U, C_{Ra}, C_{Th}, C_K and C_0 are the specific activity (in Bq/kg) of uranium, radon, thorium, potassium and other radionuclides found, respectively. If the specific activity values obtained are inserted into the above-mentioned expression, the value of 0.145 Bq/kg is calculated. On the basis both of the results of these measurements and the Requirements of the Croatian Act from the point of radiation protection [18], it could be concluded that this slag can be used as aggregate both in construction materials and building constructions.

For utilization of slag as aggregate to concrete, after the metal removal process, the crushed slag was divided into fractions of the following size: coarse (8–16 mm), medium (4–8 mm) and fine (0–4 mm). Fig. 5 shows the original particle size distribution of the slag used related to the optimum grading limits curves for concrete aggregates (marked HRN) according to the Croatian standard [13].

Table 3
Radionuclides detected in the ferrochromium slag used

Radionuclides	Specific activity, A (Bq/kg)
^{226}Ra	43.52 ± 4.41
^{214}Pb	17.39 ± 1.12
^{214}Bi	23.33 ± 4.33
^{228}Ac	8.39 ± 1.39
^{208}Tl	5.87 ± 1.05
^{40}K	41.41 ± 6.41

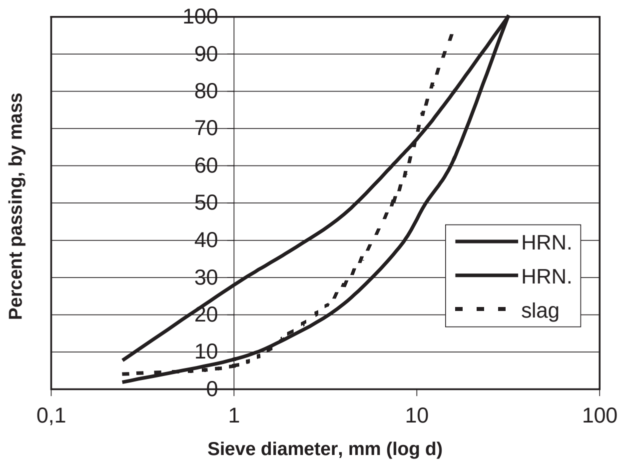

Fig. 5. The grading curve of the slag used related to the optimum grading limits curves for the concrete aggregate (marked HRN) [13].

The results indicate that the maximum grain size of the slag was 16 mm. The ratio of the amounts of individual fractions to the overall amount of the 0/16 mm fraction has been found as follows: (0–4 mm):(4–8 mm):(8–16 mm)=24:28:47, respectively. However, their ideal ratio should be approximately 50:15:35 [13]. This indicates the insufficiency of the (0–4 mm) fraction, which has to be compensated for by the crushed limestone aggregate of the same fraction. The fineness modulus of the unfractioned slag (expressed as the sum of cumulative retained on sieves of dimension # (in mm): 4.0, 8.0, 11.2, 16.0 and divided by 100) varied from 4.0 to 5.1 suggesting a too uneven granulometrical composition of the slag, as the upper acceptable limit is 3.6 [6].

It is important to note that, if slag is to be applied in concrete, a technological solution should provide grains (16–31.5 mm) as, besides improved workability, the concrete prepared with the maximum grain size of 31.5 mm always has better mechanical properties than that prepared with the maximum grain size of 16 mm, prepared, of course, under the same conditions.

Table 4 presents the physical and mechanical properties both of the slag used and of the crushed limestone aggregates relative to the Technical Requirements for concrete aggregate [5,6]. The slag compressive strength value of 88 MPa was found through experiments on the single testing cube specimen of a size 70 × 70 × 70 mm [5]. This strength is low relative to the limestone strength of 136 MPa, but it satisfies the conditions for general-purpose concretes of up to the 80 MPa (measured in dry conditions). However, it does not satisfy the Technical Requirements for wearing courses of cement concrete pavements that require a minimum strength of at least 160 MPa [5]. The low strength of the slag examined is probably due to cracking of the sample and presence of voids within the slag formed by the cooling process, and due to problems encountered in preparation of the samples for analysis; i.e., one cube of slag obtained by sawing in dry conditions was examined for compressive strength, but there were not enough large grains for preparation of samples for other tests [5]. This is why this property is examined indirectly with this aggregate type, using the Los Angeles method [14]. The results of the Los Angeles abrasion resisting test, K_{LA}=17.7%, are much better than the usual results for limestone aggregates with K_{LA}=23%. For example, the K_{LA} value for the aggregate for cement concrete slab pavements can be 18% maximum [7], which is satisfied by the ferrochromium slag, but not by the limestone aggregate. On the other hand, the value obtained for the Böhme wear resistance test of 9.5 $cm^3/50\ cm^2$ for slag in compared with 26.2 $cm^3/50\ cm^2$ for limestone also suggests the advantages of slag over limestone aggregate. It is therefore to be expected that the slag of this resistance will find its application as aggregate in all concrete types required to be wear-resistant (hydrotechnical facilities,

Table 4
Physico-mechanical properties of the slag used and of the limestone aggregates related to the Technical Requirements for concrete aggregate [5,6]

Specific properties	FeCr slag used	Technical Requirements [5]	Limestone aggregate
Compressive strength, MPa	88.00	80 min[1], 160 min[2]	136.00
The particle volume mass, kg/m^3	3250	2000–3000	2700
Adsorption of water, %	(0/4 mm) 1.05, (4/8 mm) 0.79, (8/16 mm) 0.63	1.50 max	(0/4 mm) 0.40, (4/8 mm) 0.30, (8/16 mm) 0.20
The grain shape Foury's coefficient, k	(4/8 mm) 0.17, (8/16 mm) 0.22	0.18 min, 0.20 min.	0.22–0.29
Abrasion resistance, K_{LA}, %	17.70	30.00 max[3], 22.00 max[4], 18.00 max[5]	23–29
Böhme wear resistance, $cm^3/50\ cm^2$	9.50	35.00 max[6]	26.20
Alkali-silica reaction			
The Sc–Rc graph	Harmful area	Harmless area	
Linear changes, %	(+)0.0035	(+)0.1 max	
Autoclave expansion, %	(+)0.05	(+)0.5 max	–
Frost resistance, mass loss, %	(4/8 mm) 0.40, (8/16 mm) 0.43	5.0 max[7], 3.0 max[8]	(4/8 mm) 0.50, (8/16 mm) 0.50
Granulometry: fractions mass, %	(0/4 mm) 23, (4/8 mm) 27, (8/16 mm) 45	(0/4 mm) 50, (4/8 mm) 15, (8/16 mm) 35	
Radioactivity, A, Bq/kg	0.145 (non-reactive)	$A \leq 1.0$	
Sulphur as SO_3, %	0.50	1.00 max.	
Chloride as Cl-ions, %	–	0.10 max.[9] 0.02 max.[10]	

[1]General-purpose concrete; [2]wearing courses pavements; [3]lower-layer concrete pavements; [4–5]wearing courses pavements: [4]traffic loads, [5]hard-traffic loads; [6]non-wearing concrete; [7]lower-layer concrete pavements; [8]wearing courses; [9]reinforced concrete; [10]pre-stressed concrete.

roads, industrial pavements and other wearing surfaces). The volume mass of ferrochromium slag particles is about 3250–3310 kg/m^3 and that of the limestone ones about 2700 kg/m^3. A direct consequence of the difference is the increase of the volume mass of concrete prepared with the ferrochromium slag by approximately 20–22% relative to limestone concrete, which may be an advantage or a fault, as the case may be. In standard concrete works, increased mass is obviously a fault resulting in harder manipulation in preparation and application of such concrete. The advantages will be found in concretes for underwater constructions and concretes with higher requirements for the physical properties of buildings (level of radiation, etc.).

The grain shape has been examined for (4–8 mm) and (8–16 mm) fractions. The Foury coefficients, k, obtained for both the (4–8 mm) and the (8–16 mm) fractions are 0.17 and 0.22, respectively. The lower k-values limits on the applicability of the aggregate for concrete and for pumping concrete are 0.18 and 0.20, respectively. Aggregates with the k-value lower than 0.20 are unacceptable in pumping concrete [5]. Bearing in mind the slag aggregate properties obtained, problems can be evidently expected with pumping concretes, which has been confirmed in practice. As the grain shape depends on the properties of the material and on the crushing equipment, the results obtained can be improved by proper selection of crushers.

Various methods for testing slag on the potential alkali reactivity have been used. The results obtained by chemical analysis test [9] lie below the edge of the curve dividing the Sc–Rc graph into the harmful and harmless area. However, the results of the mortar bar expansion test [10] show the linear expansion values of (+)0.0035% at 6 months, which has allowed us to classify the slag aggregate as non-reactive. The value obtained for the length change during the autoclave expansion test [11] is (+)0.05%. As the expansion limit values have not exceeded (+)0.5%, this result also suggests that there is no danger of destroying of concrete prepared with slag. The results of testing the slag for resistance to frost [12] indicate a mass loss in the (4–8 mm) and in the (8–16 mm) fractions of 0.40% and of 0.43%, respectively. The allowed mass loss for standard concretes is 12% [5]. For some constructions, the requirements are more stringent; so that the allowed mass loss for both the lower-layer concrete pavements and for the wearing courses are 5% and 3%, respectively. Ferrochromium slag evidently satisfies the most stringent conditions.

The above results of examination of slag show that the slag satisfies the criteria for production of aggregates for concretes for all traffic loads and highways [5–7]. One should point out that the standards mentioned refer to natural and crushed aggregates, and that there are no similar standards or experiences related to the slag obtained from the production of ferrochromium. There is also the issue of the appropriateness of estimation of slag applicability based on these standards relating to the natural stone materials, so that further research into and examinations of test concretes and test highway sections are proposed.

3.2. Properties of concrete made with high-carbon ferrochromium slag as aggregate

Fig. 6 shows the compressive strength development in the concrete samples (marked A–E) made with slag and limestone aggregates. Table 1 shows the compositions of the concrete samples mixtures. Fig. 6 shows that the values obtained for the 28-day compressive strength of the concrete samples marked A, B, C, D and E corresponded to the concrete brands of MB-50, MB-45, MB-40, MB-35 and MB-35, respectively. The high compressive strength at all test ages was observed in the A concrete prepared with the original unfractioned slag aggregate. The analysis of results of changes in compressive strength relative to the aggregate size indicates that the concrete prepared with the original particle size distribution of slag aggregate (sample A) has a higher compressive strength than the D concrete that was made with the slag aggregate whose particle size distribution was theoretically optimal for crushed limestone. The high compressive strength of concrete marked A has been confirmed in practice in laying a part of a cement concrete slab pavement inside the area of Ferroalloys Works in Dugi Rat, Croatia. The results obtained for compressive strength ranged from 52.7 to 55.7 MPa. This agrees well with earlier studies [19], which have confirmed that the measurements of mechanical performance in the field are much better than would be anticipated from the laboratory results.

It has also been observed that, if cement and water contents are constant, the increase in the amount of fine aggregate fraction results in a decrease of the compressive strength (the B, C and D concretes). The compressive strength development data obtained for the D concrete that was prepared with slag whose amounts of individual fractions were the same as with the crushed limestone

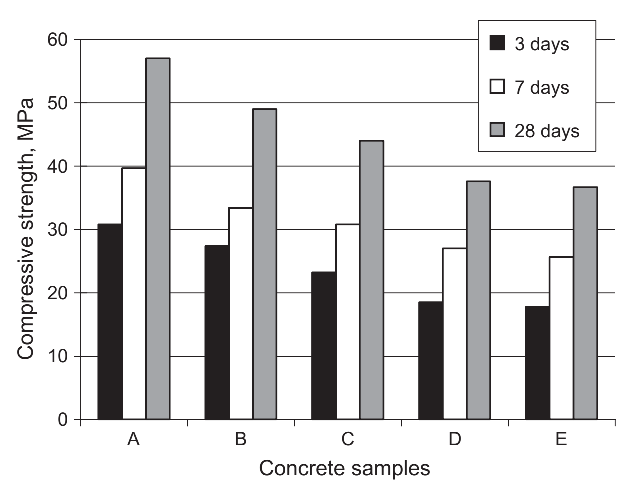

Fig. 6. Compressive strength development of the concrete samples marked A–E. Compositions of samples are given in Table 1.

aggregate of 0/4 mm:4/8 mm:8/16 mm = 52:18:30 are surprising. The values obtained correspond to the E concrete prepared with the crushed limestone aggregate although higher strength should have been expected. For that reason, the D concrete sample has been tested both for abrasion resistance and tensile splitting strength. The Los Angeles test yielded the K_{LA} value of 21.7%. This result is almost the same as for the limestone K_{LA} value of 23%, which has confirmed the low compressive strength of the D concrete. The tensile splitting strength test, determined according to the Brasilian method, showed the value of 3.96 MPa. Compared to the compressive strength value of 37.6 MPa, it is 10.5%. According to the Technical Requirements for standard limestone aggregate, everything above 10% is considered to be very good.

The A concrete sample has a 35.61% higher compressive strength than the E concrete. The Böhme wear resistance tests on A and E concretes found the values of 16.6 cm^3/50 cm^2 and 27.5 cm^3/50 cm^2, respectively. There is evidence of high wear resistance in the A concrete prepared with slag as aggregate in comparison with the E concrete made with the crushed limestone aggregate. For illustration, the wear of wearing courses in cement concrete highways must not be higher than 18 cm^3/50 cm^2 [7], which is satisfied by the slag, but not by the limestone aggregates.

These findings have suggested that the surface area of aggregate has a significant effect on mechanical properties of the concrete mortar, as pointed out in [20]. Knowing that if the grains size of aggregate increases, its specific area would decrease. Therefore, the expansion of the granulometric curve to higher grains size (to the coarse aggregate fraction) contributes to the increase of the concrete compressive strength [21]. The increase in compressive strength of the A concrete could be related both to the rough texture and the intrinsic strength of slag particles, which increases the mechanical interlocking with the cement paste in concrete, but further study is needed in order to better understand this phenomenon.

The results obtained also indicate that the mechanical properties of slag are affected by the technological process of ferrochromium production, which should be borne in mind when trying to obtain slag of uniform composition and properties.

Table 5 reports the results obtained for properties of the slag aggregate concrete relative to referent concrete with the crushed limestone aggregate. Both concretes (w/c=0.50 and 450 kg/m^3) were prepared with the aggregate of the same amount of individual fractions (0/4:4/8:8/16 = 52:18:30). A comparison of the 28-day strengths of concrete made with the ferrochrome slag aggregate, with that with crushed limestone shows that the slag concrete is stronger. Tensile splitting strength and flexural strengths measurements also showed greater values of the slag concrete than that of the limestone concrete. The module of elasticity shows similar trends to those of compressive strengths. As shown in Table 5, the concrete made with the slag aggregate is characterized by a higher volume mass, better water impermeability, abrasion, wear and frost resistance than those made with the limestone aggregate, suggesting that slag can be applied in wearing courses of concrete pavements.

Table 5
Comparison of the properties of concretes made with slag and crushed limestone as aggregates

Specific properties	Concrete with slag	Concrete with limestone
Compressive strength, MPa	66.30	52.70
Tensile splitting strength, MPa	4.80	4.25
Flexural strength, MPa	13.50	10.20
Water impermeability, mm	16.00	24.00
Los Angeles abrasion resisting, %	K_{LA}=17.70	K_{LA}=23.00
Böhme wear resistance, cm^3/50 cm^2	13.85	27.60
Frost resistance, loss of strength, %	10.00	13.00
Modulus of elasticity, GPa	39.00	34.00
Volume mass of hardened concrete, kg/m^3	2700.00	2360.00
Water absorption, mass%	0.31	0.40
Particle shape (Foury's coefficient)	0.22	0.29

The results of this study show that by using its special properties, reinforced slag concrete could be suitable for other applications, such as: for high-performance concrete for use in concrete floor slabs of industrial halls and for a hydraulic engineering constructions subjected to abrasive and corrosion environment.

4. Conclusion

From the results obtained, the following conclusions may be drawn.

Slag remains as a waste product in the production of high-carbon ferrochromium metal. By slow cooling in the air, the slag crystallizes in the form of a stable CaO–MgO–Al_2O_3–silicate product with mechanical properties similar to igneous origin rocks. Forsterite and spinel, both materials with high-melting points, are major phases in the air-cooled slag. Small amounts of enstatite and chrome-spinel are also detected.

Slag properties meet the requirements of the relevant Croatian standards prescribing the Technical Requirements for production of aggregates for concrete; as the insufficiency of the fine aggregate fraction could be compensated for by the crushed limestone aggregate of the same fraction.

All examinations of mechanical properties of both slag and reinforced slag concrete have confirmed the advantages of slag over the limestone aggregate (which is characteristic for the region of Dalmatia, Croatia) in all cases when higher quality is required from concretes than usual. Slag is particularly suitable for preparation of high concrete brands (MB-50 and higher) where the standard crushed limestone aggregate cannot provide the concrete with the desired properties.

The reinforced slag concrete is suitable for wearing courses of concrete pavements for traffic load classes 1 and

2 where carbonate stone material (limestone) mainly does not meet the Standard Technical Requirements for cement concrete slab pavements according to the Croatian standard, HRN.U.E3.020.

The use of ferrochromium slag as aggregate in concrete pavements offers a more economical solution than the standard ones, due to the very high price of stones of igneous origin, which have to be transported from distant locations.

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