THE UTILIZATION OF FERROCHROMIUM SLAG BY HYDROTHERMAL TREATMENT

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In order to transform periclase to brucite, an aqueous suspension of ferrochromium slag containing γ-C_2S, MgO and soluble chromates was hydrothermally pretreated at 150° C. Chromates present in the solution were separated. Samples to be examined were prepared from the mixtures of the pretreated slag and powdered quartz (CaO/SiO_2 = 0.85 and 1.0 resp.). They were moulded and then hydrothermally treated at 180° C. X-ray analysis, thermal and microscopic examination revealed the formation of binding products, mainly tobermorite and CSH(I) phase known for their considerable mechanical properties.

INTRODUCTION

Large quantities of slag are formed in the production of ferrochromium in the Orava ferro-alloy works Istebné. Till now there does not exist any convenient method for using this by-product. With regard to its mineralogical composition, the slag is not suitable for direct use in the manufacture of cement clinkers or blended cements of slag-portland type because of its considerable content of periclase. This by slowly hydrating to brucite expands and after the hardening of a cement structure destructs building material. Moreover, from the viewpoint of hygiene and ecology, slag is impossible to use in concrete as an aggregate because of its high content of soluble toxic chromates.

The prevailing mineralogical component of slag is γ-C_2S (approx. 80% by wt.). In contact with water it hydrates very slowly (approx 25% in 5 years) giving $Ca(OH)_2$ and the CSH phases of the low degree of crystallinity [1]. Under hydrothermal conditions and in the presence of quartz (Ca/Si = 1.5), kilchoanite and γ-C_2S hydrate are the products [2–5].

MgO (approx. 10–15% by wt.) is another component of the slag. It hydrates slowly in the presence of liquid water only on the contrary to CaO which hydrates even with vapour [6].

Under hydrothermal conditions, the hydration of periclase in binding materials depends on particle size [7]. By the hydrothermal hardening of powdered glassy slags, hydrogarnets, CSH- and Roy's phases are formed [8].

The harmful effect of periclase in cement clinkers can in some cases be eliminated by the addition of hydraulically active siliceous components [9–11] for example fly-ash. As a result of it large quantities of gel-like and disordered CSH phases are formed [12–16].

Some authors [17, 18] eliminated chromates in cement clinkers by the addition of $FeSO_4.7\ H_2O$ to a raw mixture which reduces sixvalent chromium ions to trivalent ones.

In this contribution the hydrothermal treatment of slag was studied in order to eliminate the harmful effect of MgO and to separate soluble toxic chromates. Furthermore, the hydrothermal hardening of the mixtures of pretreated slag and quartz at lower Ca/Si ratios was studied.

EXPERIMENTAL

The phase composition of starting materials and reaction products was identified by an X-ray diffractograph Philips (goniometer PW 1050, radiation CuK_α, evaluation of linear diffraction intensities according to ASTM). The chemical composition of slag was determined according to ČSN 720100. The content of soluble chromates was determined according to ČSN 830540 by the reduction of chromates in an acidic solution by gaseous SO_2 and determined gravimetrically as Cr_2O_3. Free MgO was quantitatively determined by leaching the slag in a solution of NH_4NO_3 [19], X-ray analysis via constant MgO addition according to [20] and microscopically [21–25].

The powdered slag (particle size up to 0.09 mm) and fine grained quartz (particle size up to 0.025 mm) was used. Samples were hydrothermally treated in an autoclave of commercial type and in hydrothermal bombs. The pretreatment of slag was performed in an aqueous suspension at 150°C for two days. The mixtures of pretreated slag and fine grained quartz of paste consistency (v/s = 0.3), were moulded in the shape of prisms (3×1×1 cm) or cubes (2×2×2 cm), and hydrothermally treated at 180°C for six hours. Thermal analyses were performed using MOM derivatograph (type Q 1500-D). The fracture surface topography of splinters of hydrated samples was examined by SEM (JEOL type JSM-35). The petrological analyses of the slag and the content of periclase

were determined by the polarizing microscope (Amplival pl.U).

RESULTS AND DISCUSSION

The mineralogical composition of the slag according to X-ray analysis is as follows: γ-dicalciumsilicate (γ-C_2S) prevails, there is also appreciable quantity of periclase (MgO), a small amount of merwinite (C_3MS_2), melilites (C_2AS-C_2MS_2), some spinel (MA) and contaminants (Grains of Fe, Cr, FeCr and Cr_2O_2).

The average chemical composition of the slag in % by weight of oxide is: SiO_2 24–27, Al_2O_3 4–8, CaO 48–52, MgO 8–12, Cr_2O_3 4–7, FeO about 1.0 and MnO about 0.2.

The determination of the periclase content by leaching in the solution of NH_4NO_3 depends slightly on its duration. The results of leaching are in good agreement with the X-ray results (10–12% by wt.), but they are slightly lower than the results of the microscopic examination (8–10% by wt.).

The chromium content in drinking water is given in literature [26–28]. Here its concentration is limited to 0.05 mg/l, that is 5.10^{-4} % by wt. According to [29] it is permissible only in 1.10^{-4} Cr % by wt. However Cr^{6+} content determined in this slag is 0.02% by wt. of Cr.

The hydrothermal pretreatment of the slag

From X-ray analysis it is evident that the intensity of the MgO (d_{200}) diffraction continuously decreased with the duration of the hydrothermal treatment. It was established that the complete hydration requires a temperature of 150°C and a reaction time of 1 to 2 days depending on the grain size of the slag and the rate of stirring of the suspension. The intensities of the residual unreacted γ-C_2S, merwinite and other minerals decreased considerably. In the course of hydration the phases such as $C_2SH(A)$ predominantly, brucite, hydrogarnets (C_3ASH_4), cryptocrystalline MSH (close to the serpentinic minerals) as well as some nonstoichiometric disordered CMSAH phases were formed.

Hydrothermal treatment did not affect the content of trivalent chromium ions in residual slag, that is no oxidation of Cr^{3+} to Cr^{6+} proceeded.

The hydrothermal treatment of slag-quartz mixtures

The homogenized slag-quartz mixtures with a high water to solid ratio (w/s = 10) were taken as the reference samples. The mixture of paste consistency (w/s = 0.3) were moulded into prisms or cubes. Both mixtures were hydrothermally treated at 180°C for six

Table I

Strengths of test samples

Molar ratio CaO/SiO$_2$	Strengths [MPa]	
	tensile	compressive
0.85	35.5	58.7
	33.8	65.6
	41.3	68.4
	32.6	68.2
	30.8	60.5
1.0	43.5	55.7
	37.8	63.8
	39.3	53.4
	40.8	51.5
	44.5	60.3

hours. In mixtures expressed taken as CaO/SiO_2 = 0.85 and 1.0 resp., the correspondingly small amount of quartz was taken in excess to compensate its possible interaction with periclase after hydration for a long period at room temperature.

The strength results are given in Table I. It can be seen from the comparison of the strength values that the binding strength is higher in the products with higher C/S ratio (due to the presence of xonotlite), whereas the compressive strength is higher in the product with lower C/S ratio (tobermorite).
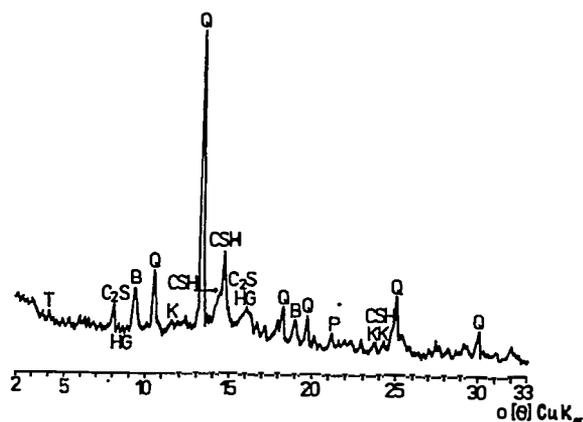
Fig. 1. Rtg. diffraction pattern of the interaction product of pretreated slag with quartz under hydrothermal conditions.
(Symbols: T – tobermorite, HG – hydrogarnets, B – brucite, Q – quartz, K – calcite, P – periclase)
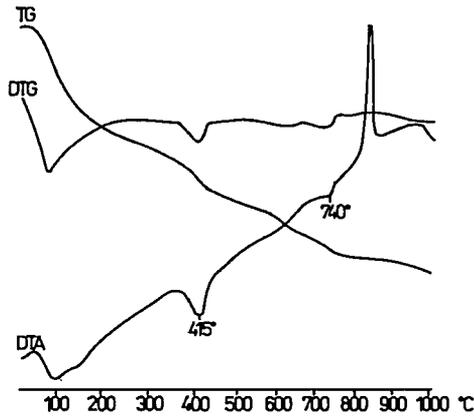
Fig. 2. Thermogram of the interaction product.

The CSH phase is predominantly formed by the interaction of pretreated slag with quartz at C/S = 0.85. Tobermorite and xonotlite resulted in smaller amounts [30]. Except for them the product contain brucite and some unreacted quartz. There are no obvious diffractions of the cryptocrystalline MSH phase of the serpentine group minerals as seen from Fig. 1. Its presence was estimated by DTA only. The mixtures with a higher water to solid ratio show, according to their powder patterns, a lesser degree of interaction.

The thermogram in Fig. 2 shows endothermic deflection corresponding to the liberation of water (110°C) and the dehydration of brucite (460°C). A typical exothermic deflection in the range of 830 to 870°C comprises the decomposition of CSH- as well as MSH phase. The shift of the deflection towards lower temperature results from the isomorphic substitution of silicon for aluminium in the CSH phase. Quartz interacts more easily with $Ca(OH)_2$ than with $Mg(OH)_2$ as was also shown by other authors [31–40].

The microstructure and the shape of the particles formed in the mixtures of paste consistency (C/S = 1.0) was examined by SEM. The fracture surface is shell-like. The foliated particles are of irregular shape with a considerable angularity typical of the honeycomb microstructure of CSH(I) phase. (Fig. 3).

CONCLUSIONS

The hydrothermal preatreatment of ferrochromium slag was applied to eliminate the harmful effect of periclase. The consequent hardening of the pretreated slag mixed with quartz resulted in a binding material with strength characteristics comparable to those of portland cement concretes. Soluble toxic chromates formed during pretreatment can be removed after the sedimentation of the suspension.

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VYUŽITIE FERROCHRÓMOVEJ TROSKY PO HYDROTERMÁLNEJ ÚPRAVE

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Ferrochrómová troska s obsahom γ-C_2S a MgO ako aj s malým množstvom toxických rozpustných chromanov sa v prvej etape hydrotermálne predupravila za vzniku $C_2SH(A)$ a $Mg(OH)_2$ – od ktorých sa po sedimentácii oddelili chromany. Vodná suspenzia produktov sa v druhej etape podrobila hydrotermálnemu vytvrdzovaniu v zmesi s mletým kremeňom, ktorý sa pridal v množstve aby mólový pomer CaO/SiO_2 bol približne 1,0. Produktom je väzná fáza CSH(I), resp. tobermoritu podobná fáza so značnými pevnosťami skúšobných trámčekov. (Rtg. difrakčný záznam, termogram, mikroštruktúra produktu uvedená na obrázkoch, tabuľka).

Obr.1. Rtg. difrakčný záznam produktu interakcie predupravenej trosky a kremeňa za hydrotermálnych podmienok.
(Symboly: T – tobermorit, HG – hydrogranát,
       B – brucit, Q – kremeň,
       K – kalcit, P – periklas).
Obr.2. Termogram produktu interakcie.
Obr.3. Typická voštinová mikroštruktúra produktu interakcie.
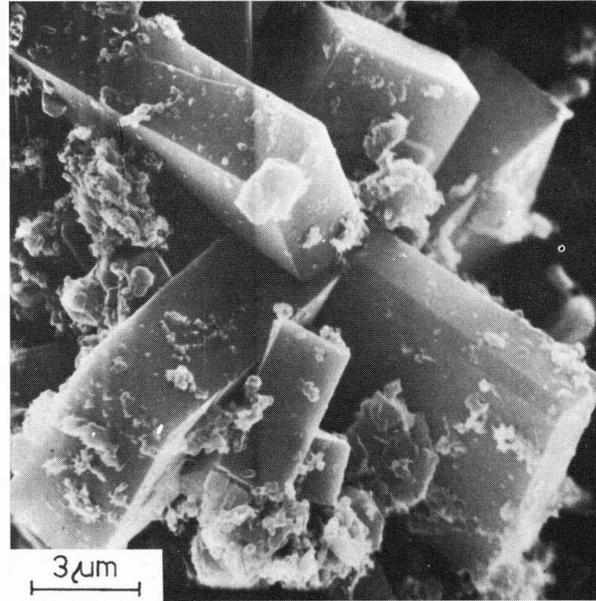
Fig. 3. Honey-comb microstructure of the interaction product.