WASTE STEEL FOUNDRY DUST AS ADMIXTURE IN BLENDED PORTLAND CEMENT

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Blended Portland cements have so far been produced with an admixture of slag, fly ash and other ingredients. The present paper surveys the results of the investigation into the properties of a new type of blended Portland cement containing waste steel foundry dust as admixture. The optimum way of preparation of this type of cement consists in the simultaneous milling of clinker, gypsum and waste steel foundry dust. The addition of the last component exerts an influence on the hydration of the blended cement.

INTRODUCTION

The production of iron and steel is accompanied by the occurrence of large quantities of secondary products (dust) containing predominantly iron oxides and, to a smaller extent, elementary iron too. Furthermore, the waste products also contain other heavy metals and, in particular, Zn and Pb which make a direct recycling of such raw materials impossible. This type of waste is mostly disposed of at waste disposal sites but such an approach is dangerous because of possible water leaching when heavy metals (Pb, Zn, Cr) [1-4] may pass into solution.

A predominant part of studies [1-7] dealing with problems associated with the waste steel foundry dust (further abbreviated as WSFD) focused predominantly on the possibility to eliminate heavy metals from the waste as well as on its subsequent recycling in metallurgical processes. Attention was also paid to conditions arising at disposal sites where such wastes are disposed of; the problems of solidification, ie the preparation of the mixtures of WSFD with portland cement and the determination of the toxicity levels of liquors leached from such mixtures [6-10] were thus tackled. The present-day blended Portland cements are made with admixtures (as per EN) of blast-oven slag, fly ashes, puzzolans, respectively SiO_2 fly ash. Very fine waste steel and foundry dust on the basis of iron oxides has not been used as admixture to blended Portland cements yet and there are no published data about the properties of this new type of blended Portland cement. Therefore, the properties of blended Portland cements containing the WSFD admixture were investigated within the framework of the present paper.

EXPERIMENTAL

WSFD rejected in the steel production in tandem furnaces and electric furnaces at Třinec and Nová Huť Ostrava (Czech Republic) were used for experiments. The above waste is separated from flue gases leaving the above furnaces by electrostatic precipitators and water mist is used afterwards to remove it as water suspension. The composition of WSFD used for experiments is given in table 1. The morphology of WAFD particles was studied with the aid of SEM with ED spectrometer as well as by using the BET method.
Blended Portland cements with WSFD admixtures were prepared in two ways:

a. By milling a mixture of clinker (see table 2 indicating the compositions of Lochkov and Hranice clinkers), gypsum and dried WSFD. The milling took place in a laboratory ball mill with a capacity of 30 liters. The required specific surface area ranged from 300 to 350 m2/kg.
b. By mechanical mixing of WSFD with Portland cement Lochkov CEM I 42.5 (see the composition in table 2). The mixture was homogenized for an hour.

Gypsum used for experiments contained 98.6 % $CaSO_4.2H_2O$.

First, the milling ability of mixtures composed of cement clinker with an admixture of 0 to 15 wt.% of WSFD (as substitution for the clinker in the cement) was determined when blended Portland cements containing WSFD admixtures were investigated. The milling ability was determined with the aid of a SEGER device (Germany) recording the consumption of the milling energy corresponding to the achieved specific surface area of the milled mixture.

Table 1. WSFD composition, (wt.%).

wt.%	Nová huť WSFD	Třinec WSFD
Fe_2O_3	77.8	85.67
ZnO	12.56	5.96
MgO	1.07	0.73
Al_2O_3	0.61	0.13
SiO_2	2.43	0.69
CaO	2.25	5.51
Cr_2O_3	0.13	0.10
CuO	0.15	0.05
CdO	0.19	0.04
PbO	2.65	0.98

Table 2. Chemical compositions of clinkers Lochkov, Hranice and PC CEM I Lochkov, (wt.).

wt.%	Clinker Hranice	Clinker Lochkov	CEM I 42.5 R Lochkov
CaO	66.81	67.14	64.03
SiO_2	22.29	21.66	20.66
Al_2O_3	5.04	4.25	4.05
Fe_2O_3	2.98	2.72	2.59
MgO	1.46	2.30	2.19
Na_2O	0.17	0.02	0.02
K_2O	1.08	1.02	0.97
SO_3	0.10	0.23	2.67

Blended cements were used for preparation of slurries characterized by the water coefficient w (w = mass of water / /Σ (mass of cement + WSFD) ranging from 0.22 to 0.35 in dependence on the rheological properties of the mixes. The setting of the mixes was determined using EN 196. Then, the hydration process of cement slurries containing the WSFD admixture was investigated in dependence on time; a semi-diabatic multi-channel calorimeter was used for this purpose. Mortars based on WSFD-containing cements were then prepared in accordance with EN 196-1. The samples made of these mortars were first kept at a temperature of 20°C for 24 hours in an atmosphere corresponding to 95 percent of relative humidity and then in water for 28 days. The samples taken out of the water bath were then kept in air (its relative humidity ranged from 35 to 45 %) and their compression strength was determined by destructive tests after periods of time ranging from 7 to 360 days. Rheological properties of mortars were assessed by pouring them on a casting table as per EN 196. The fragments obtained during the destructive testing of samples were investigated with the aid of the X-ray diffraction analysis; the morphology of fractured surfaces was studied with the aid of a SEM with ED spectrometer.

RESULTS AND DISCUSSION

Characteristics of the rejected WSFD product

WSFD particles from various plants in the Czech Republic contain lower concentrations of heavy metals (Zn in particular) as compared to WSFD data found in published papers [1-7]. This difference is due to the fact that the scope of recycling of steel plates protected by zinc coating from corrosion is still smaller in the Czech Republic than in other countries. Nevertheless, the same increase in the content of heavy metals (Zn) in WSFD as observed abroad can be expected in this country too.

WSFD particles are predominantly spherical in their character; the waste may also contain particles of irregular shapes in dependence on the steel melting technology. The RTG diffraction analysis shows that both WSFD types are composed of iron oxides; the magnetite Fe_3O_4, in addition to hematite Fe_2O_3 and traces of quartz, represents a dominant component in Nová Huť Ostrava WSFD. The hematite Fe_2O_3 predominates in Třinec WSFD in which smaller amounts of calcite, quartz and cristobalite can also be found. It is obvious from the SEM investigation into the morphology of WSFD particles that Nová Huť Ostrava WSFD consists of mostly spherical particles with dimensions ranging from 130 to 400 nm; the particles with a dimension of 180 nm occur most frequently. Třinec WSFD is composed of a mix of spherical and irregularly shaped particles with dimensions ranging from 90 to 350 nm with the largest occurrence of particles having the size of 150 nm. The specific surface area (BET) of the Nová Huť Ostrava WSFD was 8.7 m^2/g while it amounted to 4.8 m^2/g for the Třinec WSFD. Both WSFD give rise to particle agglomerates with the micro-porosity (pores < 2 nm) ranging from 30 to 38 % (as determined by BET). The character of WSFD particles is evident from figures 1 and 2.

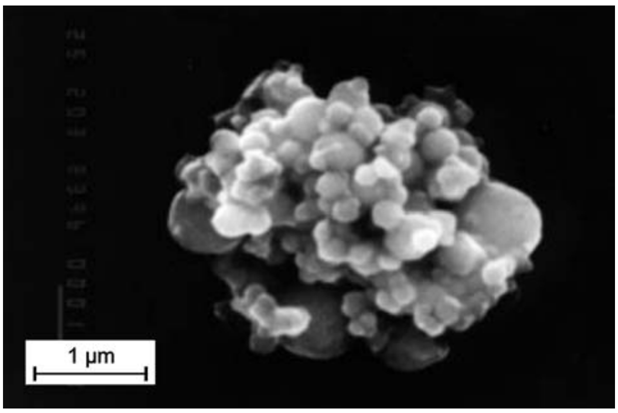

Figure 1. WSFD particle. Particle agglomeration.

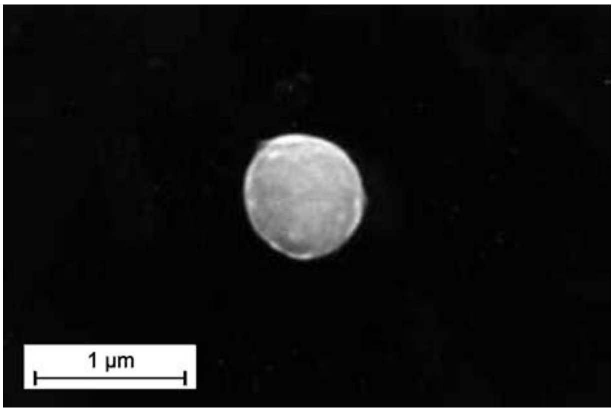

Figure 2. WSFD particle (an isolated less typical particle).

WSFD effect of the milling process of blended Portland cement

It is obvious from the results of the investigation into the milling process of the cement clinker with the admixture of fine-grained WSFD that the latter one acts as a moderate milling intensifying agent if it is milled simultaneously with portland clinker (and gypsum). With the increasing WSFD content, the value of the milling work required to achieve the given specific surface area (figure 3) drops during the milling of WSFD mixed with clinker. The obtained data show that the same character (or a better one) of the milling of Portland cement with the WSFD admixture can be expected during the commercial use as compared to the milling of the Portland cement only.

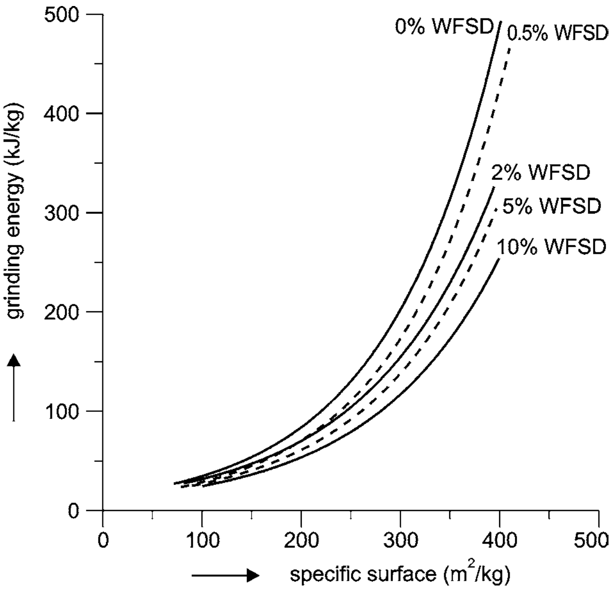

Figure 3. Dependence of the milling energy on the specific surface area of the blended cement in presence of the WSFD admixture.

WSFD effect on the hydration of blended Portland cement

The WSFD addition extends the setting of blended cement as this is evident from figures 4 and 5. This effect is obviously due to the ZnO content in the waste: the increasing content of the waste in the blended cement (over 5 wt.%) extends significantly the setting (as this was also found for portland cement [11], which may not be acceptable when used in the practice). This effect is also evident from the curves characterizing the development of the hydration heat (figures 6 and 7) in WSFD-containing slurries.

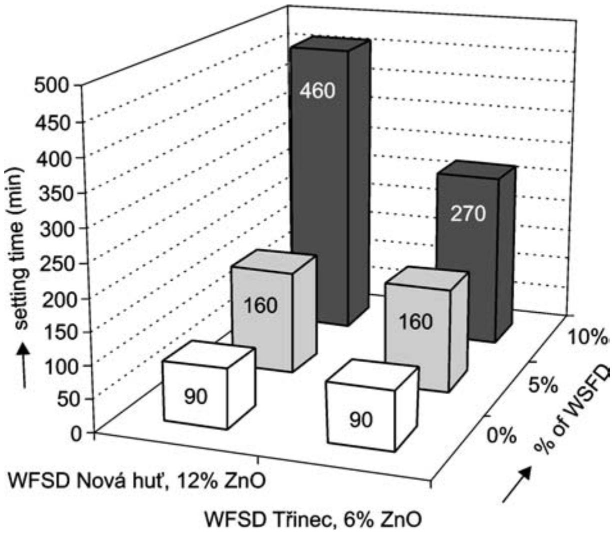

Figure 4. Dependence of the setting of cement slurries in presence of the WSFD admixture (Lochkov clinker + gypsum + WSFD).

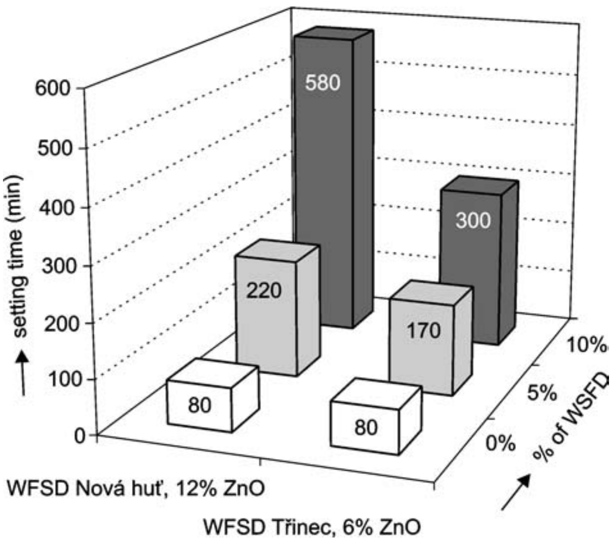

Figure 5. Dependence of the setting of cement slurries in presence of the WSFD admixture (Hranice clinker + gypsum + WSFD).

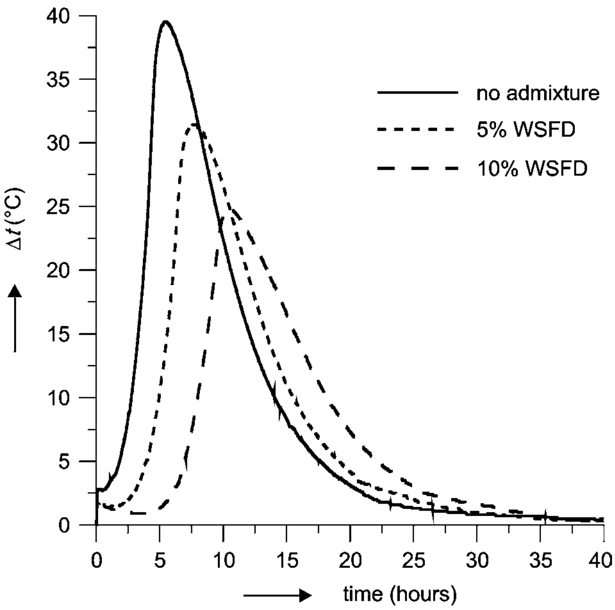

Figure 6. Time development of the hydration heat of slurries of blended cement in presence of the WSFD admixture (Lochkov clinker + Třinec WSFD - 5.9 wt.% ZnO + gypsum).

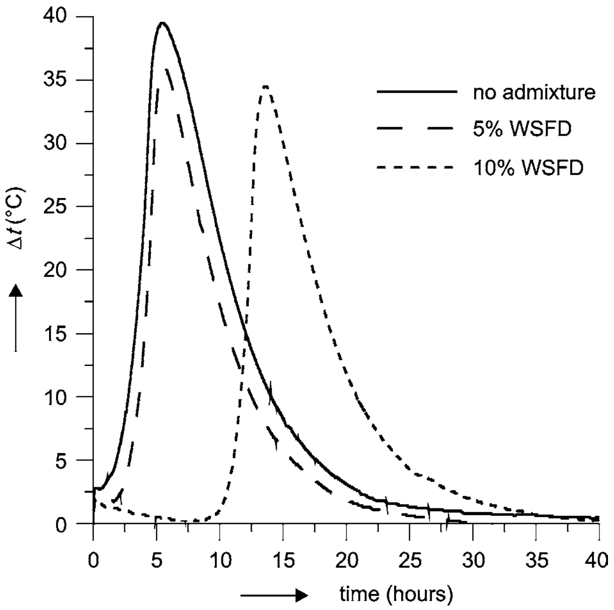

Figure 7. Time development of the hydration heat of slurries of blended cement in presence of the WSFD admixture (Lochkov clinker + Nová Huť WSFD - 12.5 wt.% ZnO + gypsum).

The WSFD addition also affects the character of the time dependences of the strength of blended cements (slurries, mortars), see figures 8 - 12. The dependences show how the strength is influenced by the method applied to the preparation of the blended cement. The following conclusions can be drawn on the basis of the results obtained:

– The strength values of blended cements prepared by mixing mechanically the individual components increase absolutely at the time horizon of 2 to 360 days. As compared to Portland cements, the strength values of these cements drop relatively at the time horizon of 2 to 360 days.
– The strength values of blended cements prepared by simultaneous milling of the individual components do not drop relatively at the time horizon of 2 to 360 days but, in some cases, these values are even higher than those characterizing the portland cement (see figures 12 and 13).
– The long-term values of strength drop only for slurries characterized by a low water coefficient.

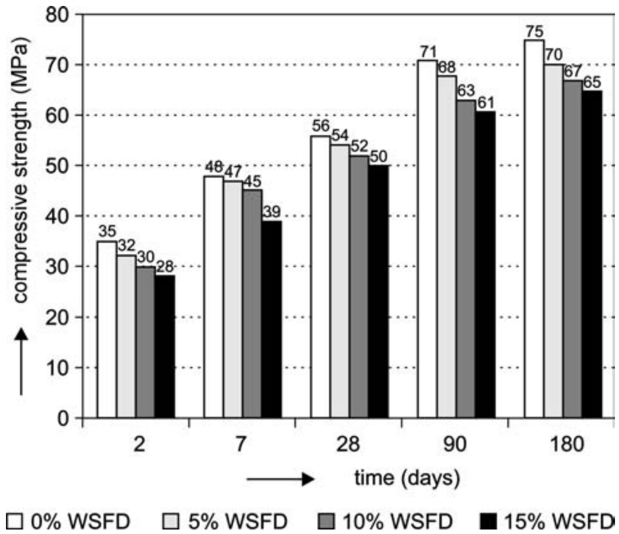

Figure 8. Time development of the strength of mortars of blended cement with the WSFD admixture (mechanical mixing of PC CEM I Lochkov clinker + Nová Huť WSFD).

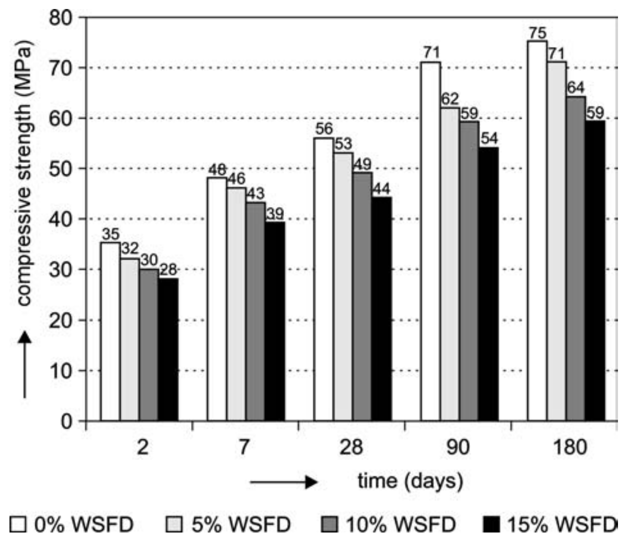

Figure 9. Time development of the strength of mortars of blended cement with the WSFD admixture (mechanical mixing of PC CEM I Lochkov clinker + Třinec WSFD).

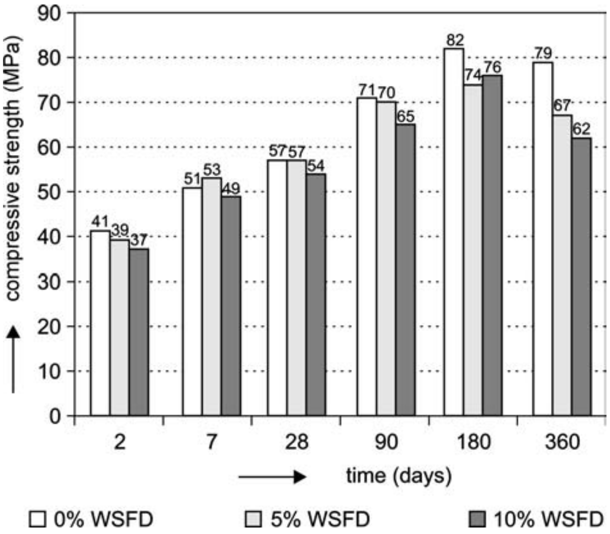

Figure 10. Time development of the strength of mortars of blended cement with the WSFD admixture (simultaneous milling of Lochkov clinker + gypsum + Nová Huť WSFD).

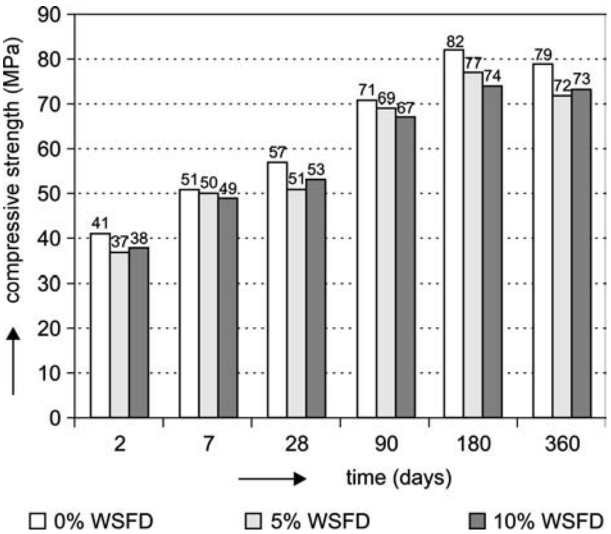

Figure 11. Time development of the strength of mortars of blended cement with the WSFD admixture (simultaneous milling of Lochkov clinker + gypsum + Třinec WSFD).

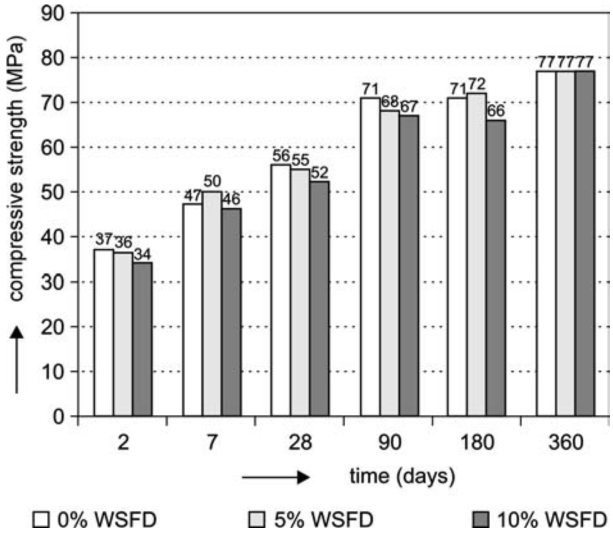

Figure 12. Time development of the strength of mortars of blended cement with the WSFD admixture (simultaneous milling of Hranice clinker + gypsum + Nová Huť WSFD).

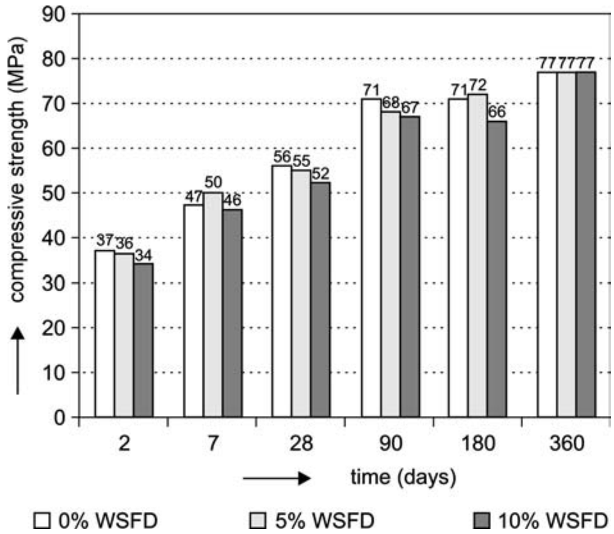

Figure 13. Time development of the strength of mortars of blended cement with the WSFD admixture (simultaneous milling of Hranice clinker + gypsum + Třinec WSFD).

It is obvious from the results showing the time development of the strength at the horizon of 360 days that the simultanous milling of clinker, gypsum and WSFD represents the optimum way of preparation of blended cements. This is probably due to a better distribution of the WSFD component in the body of the blended cement.

Fe_2O_3, respectively Fe_3O_4 (predominating in the WSFD composition) does not practically play any paper in the hydration process of cement. WSFD particles are entrenched in the structure of hydrates (C-S-H phase), see figure 14. The reaction of Fe_2O_3 with $Ca(OH)_2$ giving rise to hydrates of the type C_4FH_n in the aqueous environment is rather improbable from the thermodynamic point of view as this is substantiated by published data [12,13]. Fe_2O_3, respectively Fe_3O_4 may react theoretically in the cement suspension in presence of $Ca(OH)_2$ and $CaSO_4.2\ H_2O$ by giving rise to an expansive compound $C_6F\bar{S}_3H_{32}$ (analogous to the ettringite). It is evident from published data [12,13] that the viability of the reaction giving rise to $C_6F\bar{S}_3H_{32}$ is dependent on kinetic conditions, and it is low. No hydration products of the type C_4FH_n and $C_6F\bar{S}_3H_{32}$ (figure 15) were found during the investigation into the hydration products occurring in hard-set mixes of WSFD with portland cement. The formation of the thaumasite $C_3S\overline{CS}H_{15}$ represents another potentially viable reaction associated with the ferric compounds. This hydrate [14] is formed during a slow oxidation of FeS_2 in the environment of the hard-set cement stone. In this case, a reaction takes place when very fine Fe_2O_3 and H_2SO_4 are formed from FeS_2. H_2SO_4 reacts with calcium hydrates and $CaCO_3$ in the hard-set cement stone. The forming secondary $CaSO_4.2H_2O$ may then react with the C-S-H phase and $CaCO_3$ and give rise to thaumasite $C_3S\overline{CS}H_{15}$ if the pH value of the environment is about 12.5; this process eventually results in the destruction of the concrete [14]. However, this reaction is quite improbable in the case of WSFD investigated in this paper because the waste in question does not contain any FeS_2. The RTG analysis did not demonstrate any presence of the thaumasite in hydrated mixes of Portland cement with WSFD.

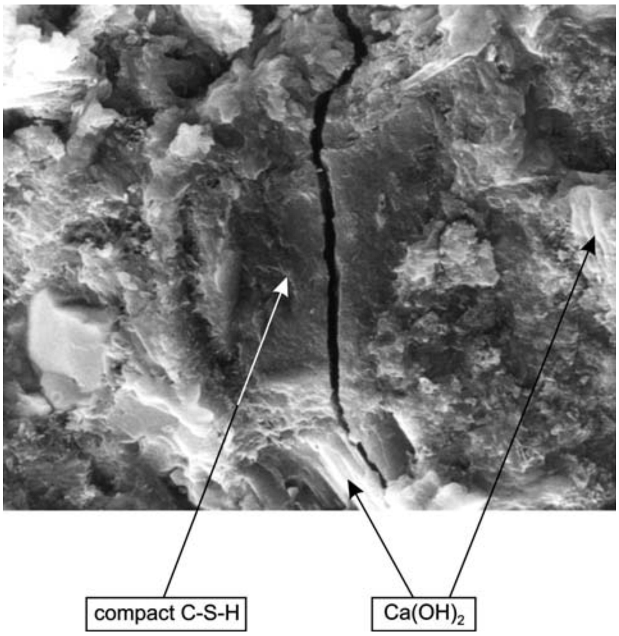

Figure 14. Fracture surface of the hard-set slurry of blended cement with the WSFD admixture after 28 hydration (90 wt.% CEMI Lochkov clinker + 10 wt.% Třinec WSFD), w = 0.32.

Nevertheless, a large specific surface area of WSFD particles may accelerate the nucleation of the C-S-H phase. In this way, even WSFD may play an active paper in the hydration process of cements. The decrease or the stagnation in the strength values of the WSFD mixtures with portland cements is probably due to the presence of ZnO in the waste matter, and not to the formation of expansive compounds of the type $C_6F\overline{S}_3H_{32}$ and $C_3S\overline{CS}H_{15}$. No expansive hydration products were detected during the investigation into the composition of hydration products in the mixes characterized by dropping strength values but traces of zinc compounds of the type $CaZn_2(OH)_6.2H_2O$ could be observed. Such compounds were found at the fracture surface in the proximity of the WSFD particles in the body of the C-S-H phase. "Untypical" forms of the C-S-H phase could also be found at the fracture surfaces of hard-set mixes characterized by falling strength.

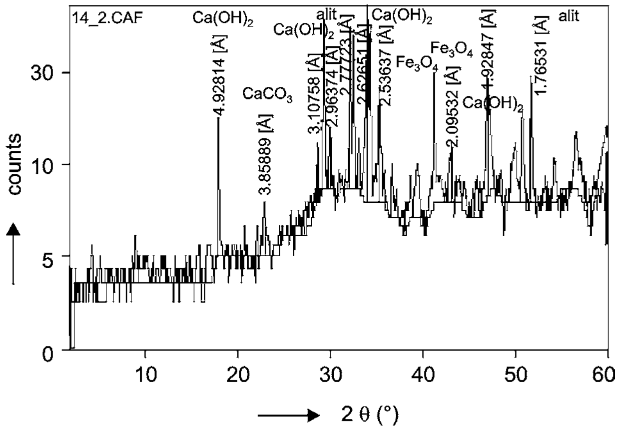

Figure 15. XRD pattern of hard-set slurry of blended cement after 28 hydration days (CEM I Lochkov clinker + Třinec WSFD), w = 0.32.

CONCLUSIONS

Following qualitative technological conclusions can be drawn on the basis of the results obtained:

1. The use of WSFD as a part of blended cements is probably viable. Up to 10 to 15 % of WSFD can be used to substitute the clinker.
2. Blended cement should be produced by simultaneous milling of the clinker, WSFD and gypsum.
3. ZnO content in WSFD is expected to exert a negative effect on the propeties of blended cements.
4. The most suitable type of clinker for the manufacture of blended cement will have to be identified.

Acknowledgement

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ODPADNÍ OCELÁRENSKÉ ÚLETY JAKO PŘÍSADA DO SMĚSNÝCH PORTLANDSKÝCH CEMENTŮ

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Přísadu vysoce jemných odpadních ocelárenských úletů na bázi oxidů Fe lze pravděpodobně použít jako přísadu do směsného portlandského cementu do obsahu 10-15 hmot.% jako náhradu slínku. Přísada úletů positivně ovlivňuje proces mletí, kdy působí jako mírný intenzifikátor mletí. Z hlediska studia pevností malt v časovém horizontu až 360 dní je jako optimální způsob přípravy směsného cementu současné semílání slínku, úletu a sádrovce. Částice přísady úletu (oxidy Fe) se prakticky vůbec nezúčastňují procesu hydratace, kdy nebyly identifikovány Fe hydráty. Vysoký měrný povrch částic úletu může způsobovat urychlení nukleace fáze C-S-H a tím pozitivně ovlivnit proces hydratace. Vlastnosti směsného cmentu negativně ovlivňuje obsah ZnO v úletech.