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Solidification of waste steel foundry dust with Portland cement

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Abstract

Properties of mixtures of Portland cements and "waste steel foundry dust (WSFD)" from Czech steel works were examined. It was found that WSFDs are formed by microporous clusters of spherical particles of iron oxides, ranging in size from 10 to 100 nm. The content of ZnO in WSFD affects markedly the hydration of cement + WSFD mixtures both in solidification time and strength development. Properties of WSFD are very similar to those of very fine silicon flue dusts formed during Si and FeSi production. Cement + WSFD mixtures show long term strength stability and low heavy metals leaching even at WSFD content of 70–80 wt.% The above results document the perspectives of WSFD solidification, disposal and the use of this waste material as a new additive to building materials. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solidification; Foundry dust; Cement; Material properties; Leaching

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1. Introduction

Iron and steel production generates large quantities of a byproducts (flue dusts) that are mainly landfilled and only seldom further utilised. The wastes from iron and steel production contain Fe oxides as a dominant component and to a smaller extent also Fe metal. Other heavy metals contained in these wastes are in particular Zn and Pb, which impede their recycling. These wastes are hazardous because of potential leaching of their heavy metals (Pb, Zn, Cr) [1,2,5].

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Table 1
Chemical composition of waste steel foundry dust used in experiments

wt. (%)	Třinec dust	Nová hut' dust
Fe total	65.8	55.7
Fe metal.	0.98	0.18
SiO_2	7.1	1.42
CaO	11.1	2.64
MgO	2.35	0.79
Al_2O_3	1.28	0.22
ZnO	0.81	6.49
Ni	0.001	0.012
Cr	0.016	0.1
V	0.004	0.006
MnO	0.49	1.25
C common	1.77	0.75
As	0.0000060	0.000049
Cd	0.000043	0.00393
Cu	0.000005	0.00743
Pb	0.00136	0.00176

Most studies [1] dealing with problems of waste steel foundry dusts (referred to hereafter as WSFD) centred on the elimination of heavy metals from these dusts and their subsequent recycling in metallurgical processes. Other researchers works [2–6] were concerned with landfilling conditions, with studying the problem of solidification, i.e. the formation of WSFD + Portland cement mixtures and the evaluation of the toxicity of the leachates.

The present work deals with the properties of materials prepared from Portland cements and WSFD from Czech localities. Special attention has been paid to the pastes, i.e. to aqueous suspensions of cements and WSFD. Additional research, the results of which will be published later,[1] will focus on the properties of mortars and concretes with WSFD additives.

2. Materials and methods

The experiments were carried out with WSFD samples from iron and steel production in the steel works of Třinec (blast furnace flue dust) and Nová hut'—Vítkovice (steel foundry flue dust). These WSFD dusts were obtained from the waste gases collected in an electrostatic precipitator after their condensation with water mist as aqueous suspensions. The compositions are given in Table 1.

The materials (mixtures) containing WSFD were formed using of standard Portland cements produced in the Czech Republic. The composition of these cements (Table 2) complied with the European standard ENV 196.

WSFD + cement mixtures were prepared such that dried WSFD was mechanically homogenised with a given cement and then pastes with a required water coefficient $w =$ mass

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[1] Unpublished results of project. "Re-evaluation of dangerous waste on the basis of ferric oxides with portion of heavy metals as a new additive to building materials."

Table 2
Portland cements used in experiments

Hranice CEM I 42.5	Hranice CEM II/A-S 42.5	Hranice CEM II/B-S 32.5 R	Lochkov CEM I 42.5	Lochkov CEM II 32.5	Prachovice CEM I 42.5 R	Čížkovice CEM II/A-S 42.5 R
Standard Portland cement	Slag blended Portland cement	Slag blended Portland cement	Standard Portland cement	Slag blended Portland cement	Standard Portland cement	Slag blended Portland cement

of water/(mass of cement + WSFD) were formed using a mixer. The water coefficient of these mixtures ranged from 0.29 to 0.45, depending on their rheological properties. WSFD content in the WSFD + cement mixtures varied from 0 to 80 wt.%

The study of the materials formed from WSFD + cement mixtures involved the examination of the rheological properties of the mixtures (suspensions) by measuring their viscosity and flow limits with a rotary viscometer. Compressive strength measurements of prepared WSFD + cement mixtures were performed with cubic testpieces of 2 cm × 2 cm × 2 cm dimensions, which were first maintained at 20°C for 24 h in moist air (95% relative humidity) and water for 28 days and then stored in air with 35–45% relative humidity. At time intervals within a 7–360-day period, the compressive strengths of these testpieces was determined destructively. The splits formed in these destructive tests were used to study the composition of the hydration products by X-ray analysis, their morphology by scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDX) and by high pressure mercury porosimetry. The morphology of WSFD particles was examined by SEM and by absorption analysis (BET). The hardened WSFD + cement mixtures (after 28-day hydration) were subjected to leaching tests [8] based on one-day leaching of the sample with water, using a solid phase to water ratio = 1:10 and 5–10 revolutions of the vessel made of an inert material. The content of heavy metals in the filtrate of the leachate was determined by atomic absorption spectroscopy (AAS).

3. Results and discussion

The results obtained in this study show that the WSFD particles from Czech localities contain heavy metals (in particular Zn) in lower amounts compared to WSFDs reported elsewhere [1–6]. This difference is due to the fact that in the Czech Republic the recycling of steel sheets with Zn anticorrosion protection is less extensive than in other countries. Nevertheless, a similar increase of heavy metals (Zn) content in WSFDs is expected to occur in the near future also in this country.

WSFD particles have mainly a spherical shape, but depending on the steel melting technology, part of them can be also irregular. The X-ray diffraction analysis shows that both WSFD samples are composed of Fe oxides (Fig. 1). The dominant component of Nová hut' WSFD is magnetite (Fe_3O_4), with smaller amount of hematite (Fe_2O_3) and traces of quartz, while in Třinec WSFD the prevailing is Fe_2O_3, with smaller amounts of calcite, quartz and cristobalite. From the study of the morphology of WSFD by SEM it follows that WSFD Nová hut' contains mainly spherical particles of 130–400 nm size, with 180 nm particles

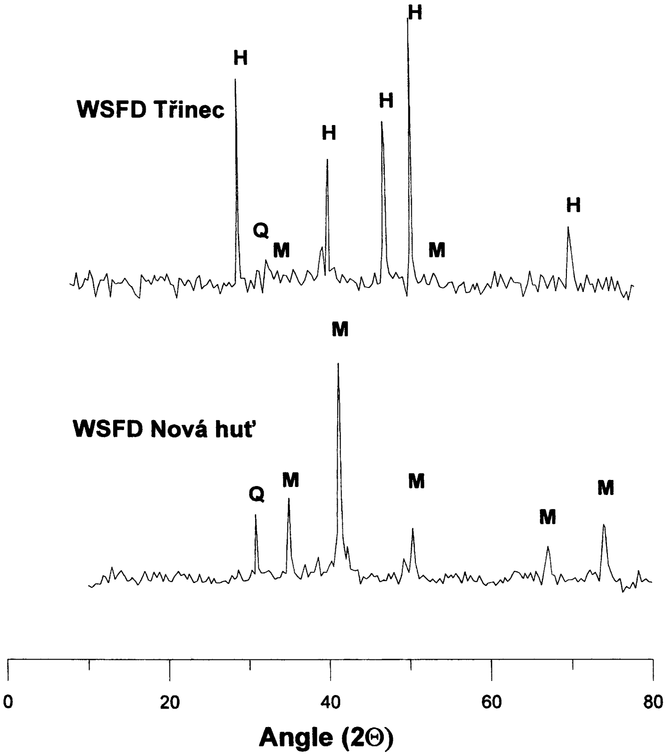
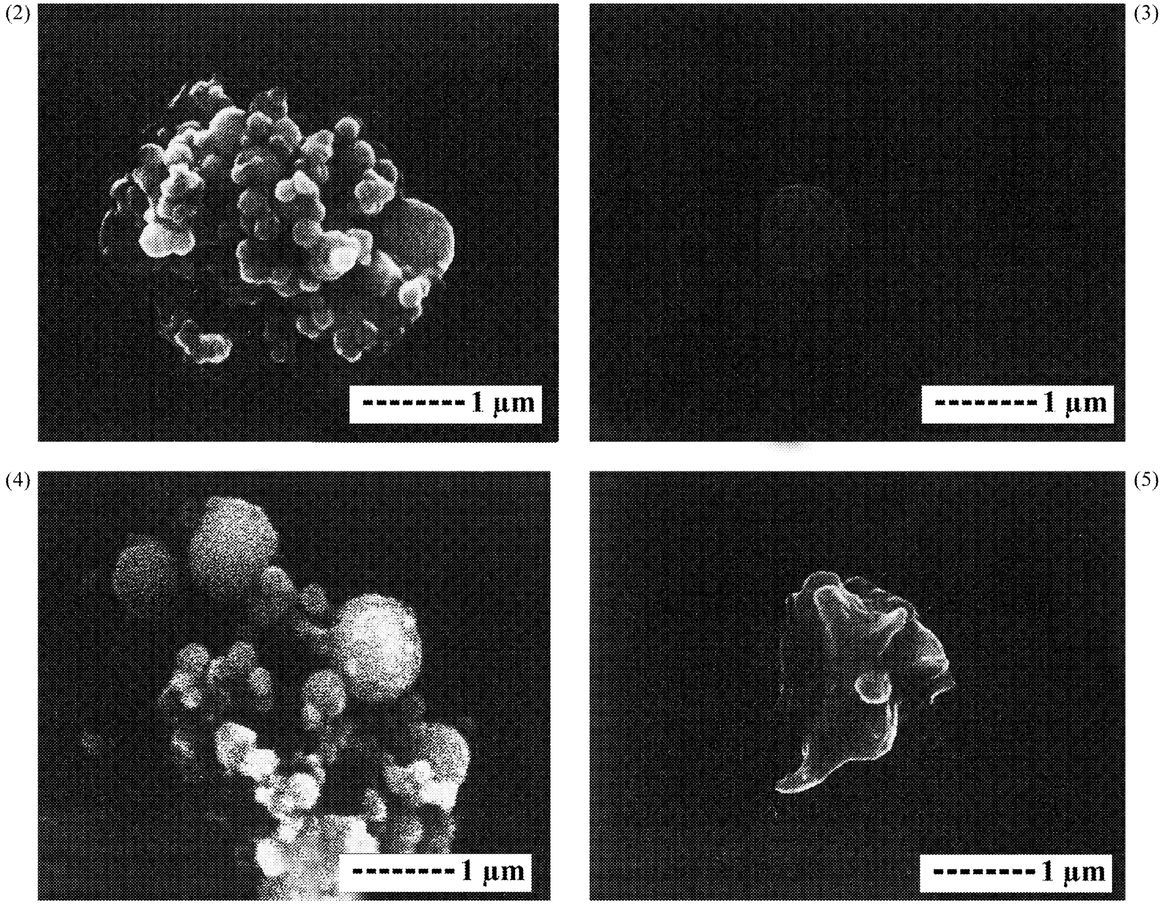


Fig. 1. X-ray diffraction pattern Steel foundry dust Nová hut', H; hematite, M; magnetite, Q; quartz.

being dominant. Třinec WSFD consists of 90–350 nm spherical and irregular particles, with predominant fraction of 150 nm particles. The specific surface (BET) of Nová hut' WSFD was 8.7 m^2/g while that of Třinec WSFD was 4.8 m^2/g. The particles of both WSFDs form clusters of 30–38% microporosity (pores $<$ 2 nm, BET). Nová hut' and Třinec. WSFD particles are shown in Figs. 2–5.

The property of WSFD + cement mixture measurements have led to a certain differentiation of these mixtures in that the mixtures with higher than 50–60% WSFD are considered "solidificates" (products of solidification/stabilisation process), while the materials with the lower WSFD content (5–15 wt.%) are regarded as "building materials".

Figs. 6–8 show selected results of strength measurements of "solidificates" performed during the 7–360-day period. The results document that one can prepare the mixtures (pastes) with high WSFD content and low water coefficient. It was further found that the strength of the hardened WSFD + cement mixtures (to 65% of WSFD content) is stabilised even after longer time interval than the 1-year interval just mentioned. The study of "solidificates" has manifested a significant difference between WSFD Třinec and Nová hut' samples in that the strength of the mixtures formed from WSFD Třinec was considerably higher compared to the mixtures containing WSFD Nová hut'. Furthermore, "solidificates" from WSFD Nová hut' containing more than 60% WSFD and some kinds of



Figs. 2–5. (2) Particles (cluster) of steel foundry dust Nová hut', SEM. (3) Typical spherical particle of steel foundry dust Nová hut', SEM. (4) Particles (cluster) of steel foundry dust Třinec, SEM. (5) Asymmetric particle of steel foundry dust Třinec, SEM.

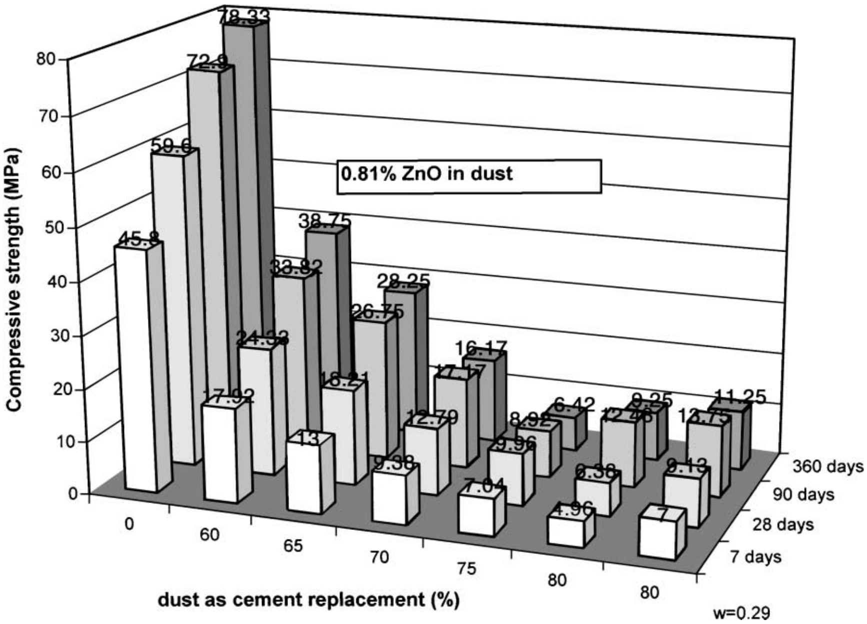


Fig. 6. Strength development of solidified steel foundry dust Třinec + PC Lochkov CEM I 42.5, $w = 0.32$.

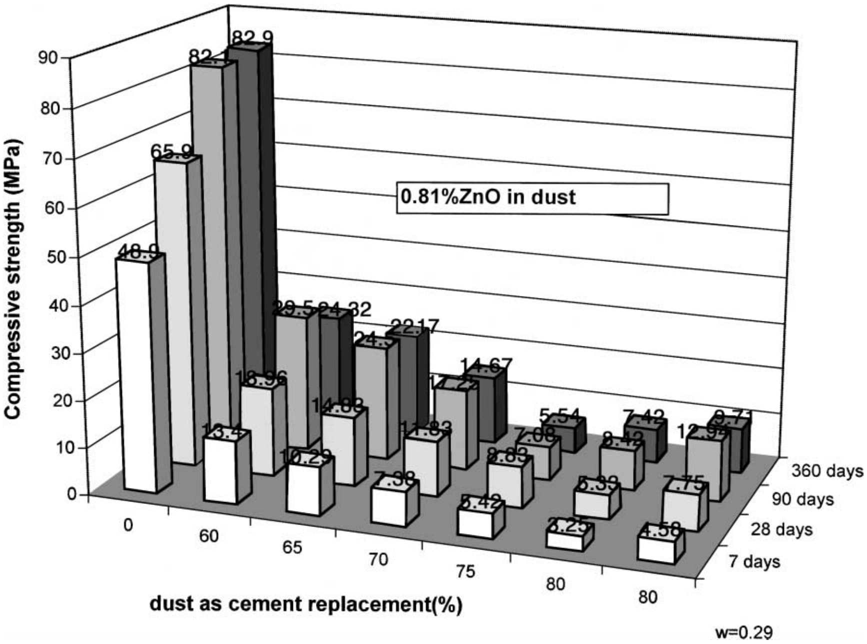


Fig. 7. Strength development of solidified steel foundry dust Třinec + PC Čížkovice CEM II A/S 42.5 R, $w = 0.32$.

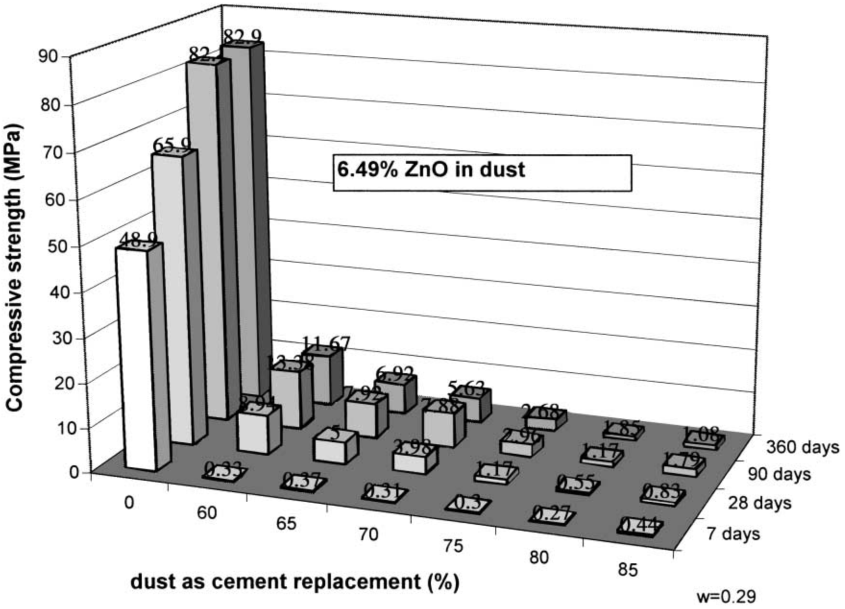


Fig. 8. Strength development of solidified steel foundry dust Nová hut’ + PC Čížkovice CEM II A/S 42.5 R, $w = 0.32$.

cements (Lochkov and Hranice) were characterised by an extremely long solidification time (longer than 3–5 days). The only exceptions were Čížkovice and Prachovice cements where “solidificates” gave satisfactory results. This difference results obviously from the different Zn content in both WSFD samples, where Zn is present as ZnO. The oxide unfavourably affects the hydration of Portland cement by postponing the start of solidification and lowering the strength of the WSFD and cement mixtures. The effect of ZnO is caused by the reaction of ZnO with $Ca(OH)_2$ to form the low solubilty zinconates [8]. The cements with rapid strength increase and those with the slower $Ca(OH)_2$ formation (such as Čížkovice and Prachovice cements) are not evidently as sensitive to this effect, as documented by the satisfactory results obtained with these materials.

The measurements of rheological properties of WSFD and cement mixtures revealed of minima in the curves of viscosity on WSFD content (Fig. 9). The improvement of rheological properties is caused by filling up the space between cement particles with much smaller WSFD particles.

Figs. 10–13 present selected results of mechanical strength of measurement for hardened cement pastes containing less than 15 wt.% WSFD. The WSFD is regarded as an additive to the cement or as its replacement. The results show that additions of up to 15 wt.% WSFD to Portland cement do not cause any significant loss of the strentgh of the mixture. In some cases we observed a strength increase. The time dependence of the strength development of these mixtures depends not only on ZnO content but likely also on the kind of Fe oxides present in WSFD.

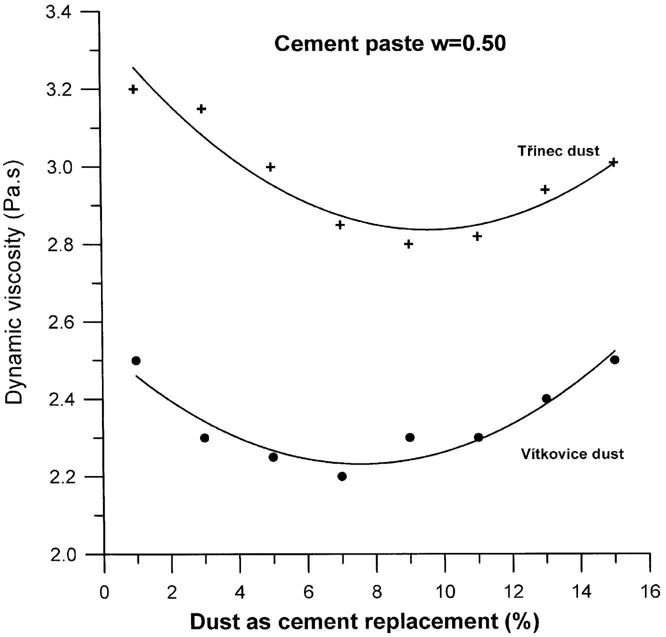


Fig. 9. Rheological properties of cement pastes with steel foundry dust.

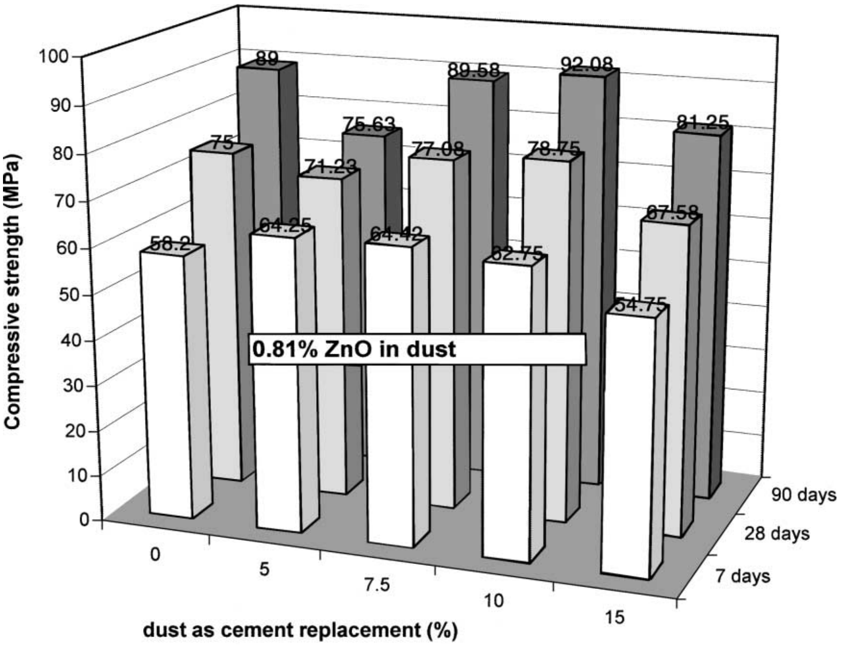


Fig. 10. Cement pastes with steel foundry dust Třinec + PC Čížkovice CEM II A/S 42.5 R, $w = 0.30$.

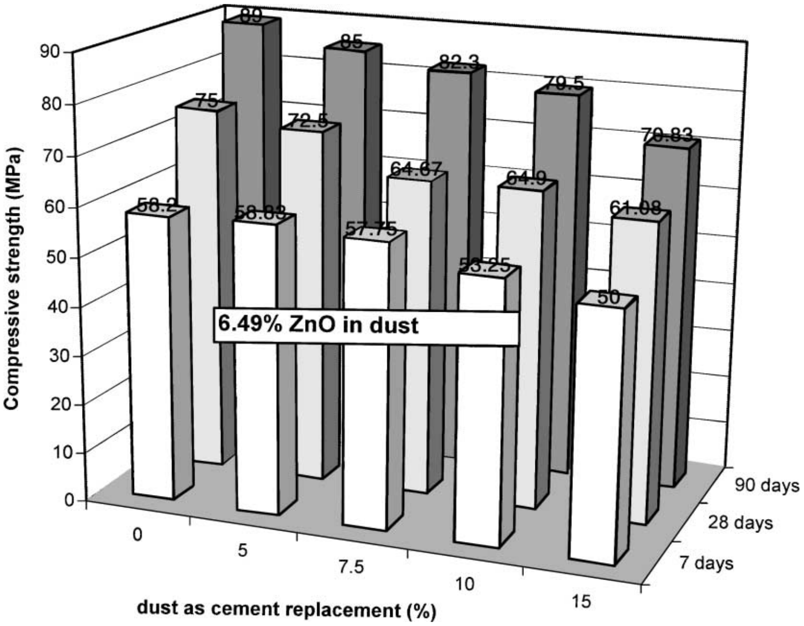


Fig. 11. Cement pastes with steel foundry dust Nová hut' + PC Čížkovice CEM II A/S 42.5 R, $w = 0.30$.

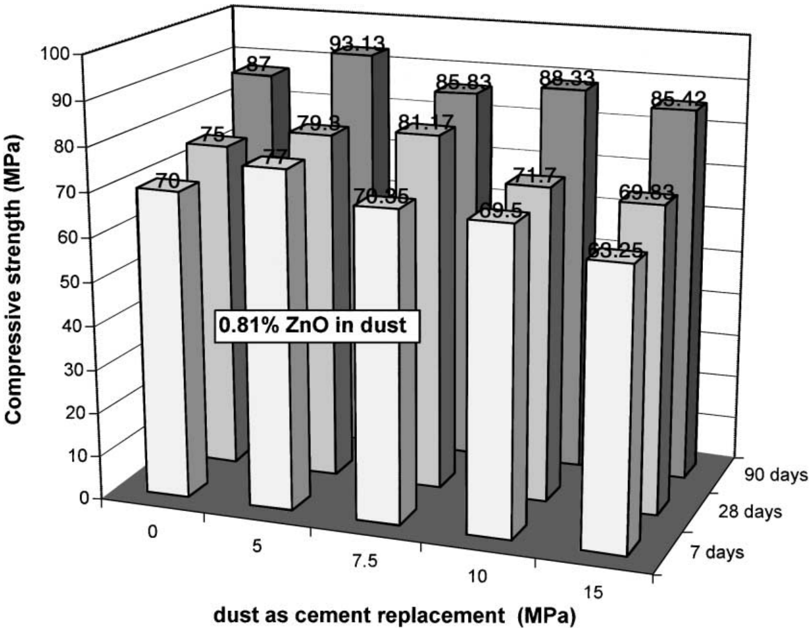


Fig. 12. Cement pastes with steel foundry dust Třinec + PC Hranice CEM I 42.5, $w = 0.30$.

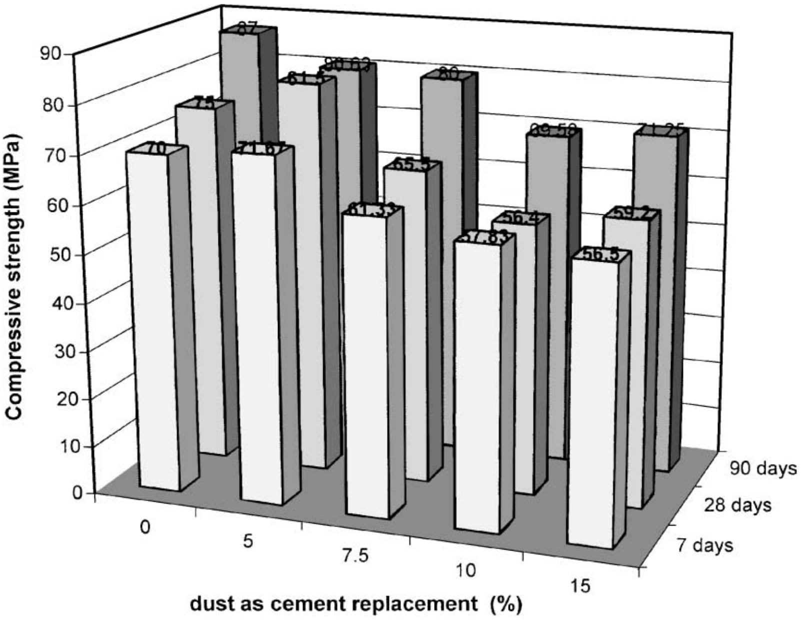


Fig. 13. Cement pastes with steel foundry dust Nová hut' + PC Hranice CEM I 42.5, $w = 0.30$.

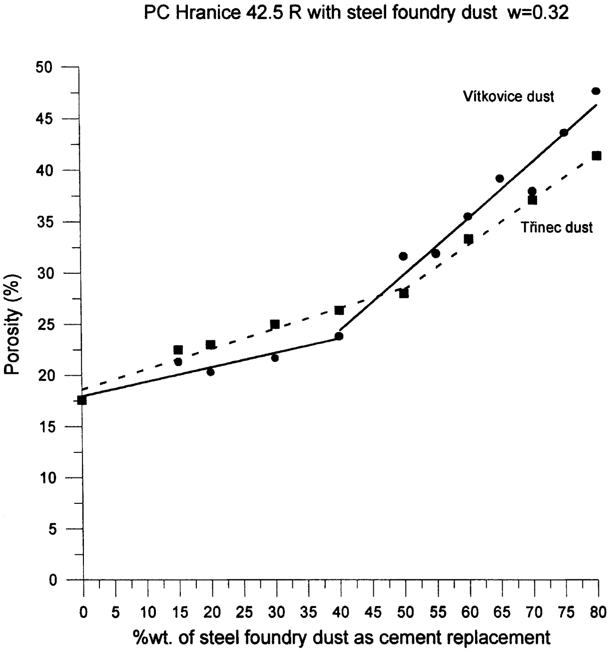


Fig. 14. Porosity of hardened cement pastes PC Hranice 42.5 R with steel foundry dust, $w = 0.32$.

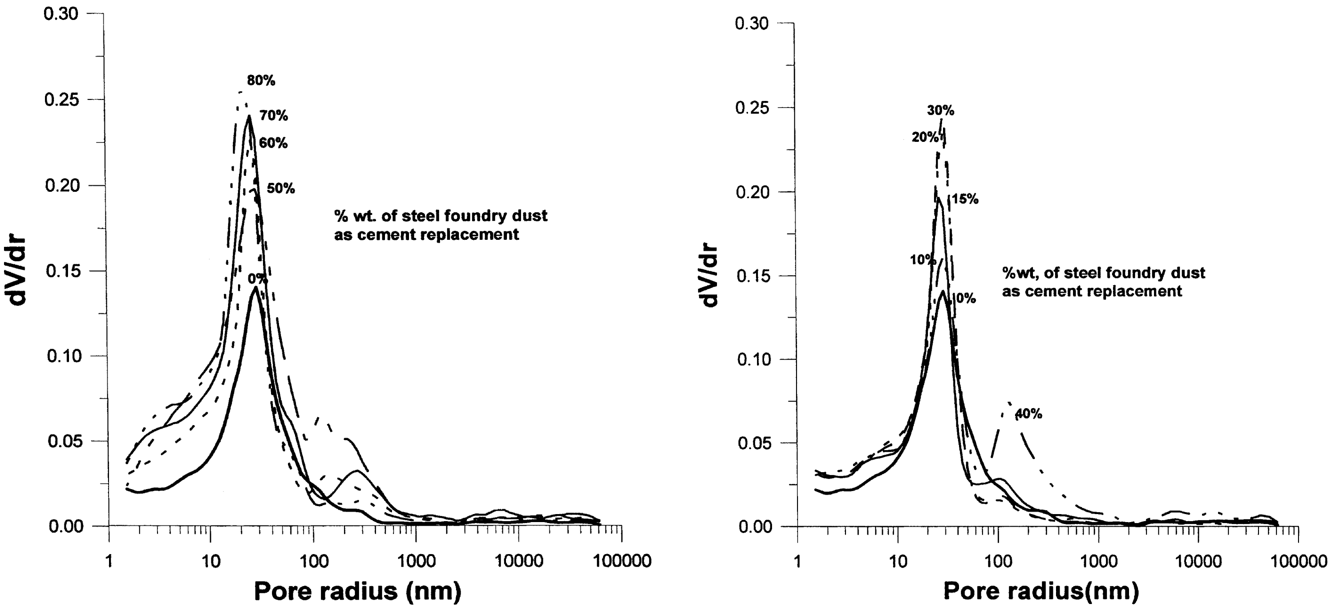
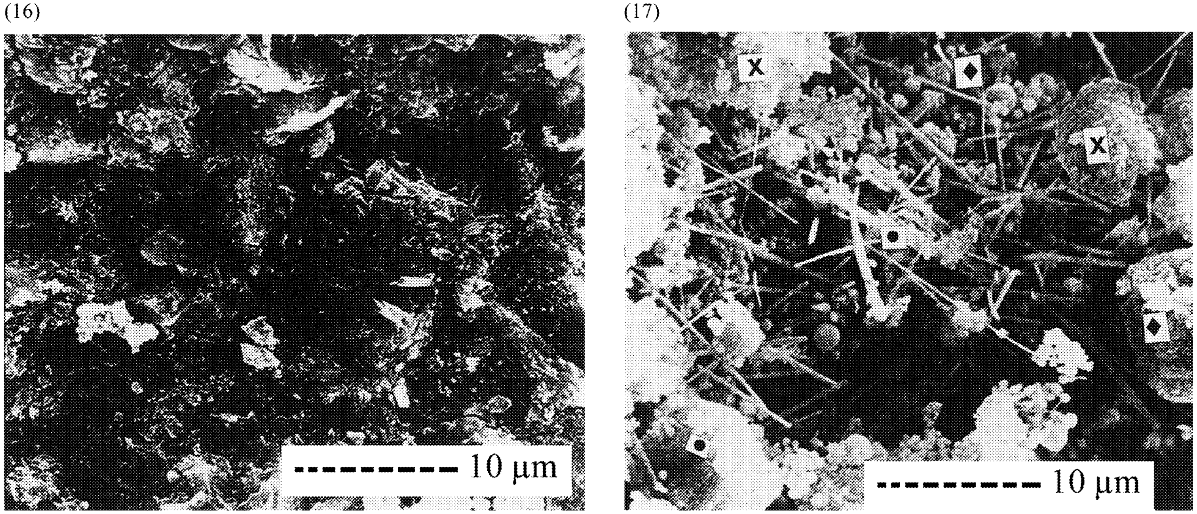


Fig. 15. Pore distribution of hardened cement paste PC Hranice 42.5 R with steel foundry dust, $w = 0.32$.



Figs. 16 and 17. (16) Microstructure of hardened cement paste with 15% of steel foundry dust Nová hut', compact C–S–H phase with Ca(OH)$_2$, SEM. (17) Microstructure of hardened cement paste with 80% of steel foundry dust Nová hut', x: C–S–H phase, (●): Ca(OH)$_2$, (◆): cluster of dust particles, SEM; EDX analysis of needles: Ca; Si, Al and Zn not detected; EDX analysis of spheres: Ca and Fe; Zn not detected.

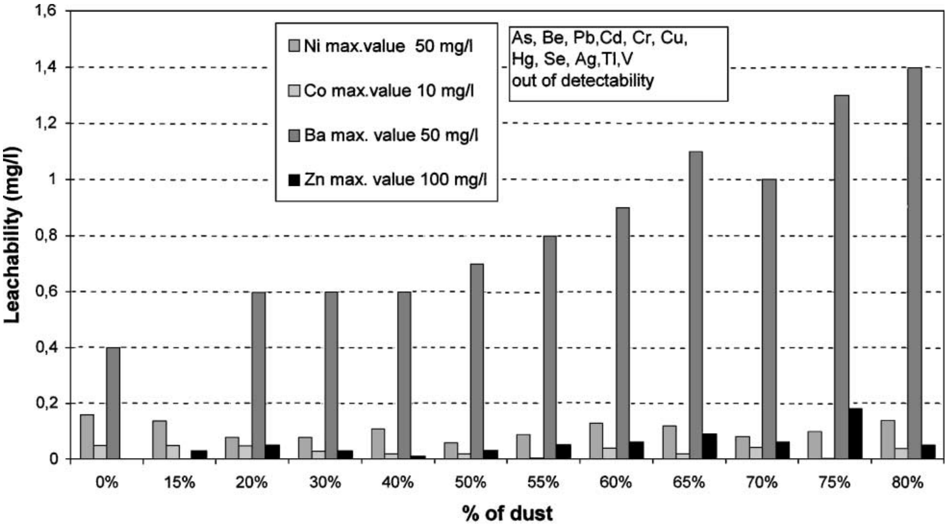


Fig. 18. Leachability of hardened cement paste PC Hranice with steel foundry dust Nová hut' (6.49% ZnO), $w = 0.32$.

The study of the morphology of the hardened WSFD and cement mixtures allowed us to conclude that the slow increase of total porosity with increasing WSFD content in the mixture (Fig. 14) can be related to the microporosity of compact WSFD clusters. If WSFD content exceeds 40 wt.%, the increase in the total porosity of hardened mixtures becomes much greater. The pore distribution curves for the hardened WSFD and cement mixtures show inceasing dependence on WSFD content (Fig. 15).

The fracture surfaces (Figs. 16 and 17) of the hardened WSFD and cement mixtures with low WSFD content (up to 25–30%) do not show discernible differences from those of the hardened Portland cements. The detection of WSFD particles in the mass of calcium hydrosilicates (further only C–S–H phase) and $Ca(OH)_2$ on the fracture surfaces is not possible. On the other hand, on the fracture surfaces of the hardened "solidificates" (containing more than 50–60% WSFD), individual WSFD particles and their clusters, are discernible, but these are covered by layers of $Ca(OH)_2$ (converted subsequently to $CaCO_3$).

Leaching tests (Fig. 18) yielded very low concentration of heavy metals in the leachates of the materials with up to 80 wt.% WSFD. Heavy metal concentrations in the leachates are thus markedly below the limits determined for nonhazardous leachates [7]. Our results agree well with the studies in which a nonhazardous character of the leachates from hardened WSFD + Portland cements had been proved for the mixtures with up to 70% WSFD containing 30–45% ZnO [4].

WSFDs from steel works are similar to some other flow dusts, namely to "silica fume" (hereafter referred as SF) from Si and FeSi production. SF contains amorphous spherical particles (clusters) of SiO_2 having very similar dimensions and morphology as WSFD. Nowadays, SF is used as an important additive to blast furnace cements [9]. The similarity of WSFD and SF manifests itself both in their ability to fill up the space between much larger cement particles (filler effect) and in their participation in the hydration process taking place during cement hardening. In the course of cement hydration, fine SF particles react with $Ca(OH)_2$ on the C–S–H phase, contributing thus to its strength increase. Fe_2O_3 and Fe_3O_4 in WSFD do not react with $Ca(OH)_2$, but the high specific surface of WSFD particles likely speeds up the nucleation of the C–S–H phase. In this way, WSFD becomes involved in the process of cement hydration. Time dependences of the strength development of WSFD and cement mixtures corroborate this assumption, as the strength of these mixtures does not decrease with increasing content of WSFD (as cement replacement) in the mixtures (up to a certain limit) and in some cases it even increases.

In another stage of our research (footnote 1) we have shown that WSFD additives show favourable effects on the properties of cement mortars and concretes and verified the possibility of the replacement of cement by 15–20% of fine WSFD in these building materials (long term stability of strength). The results of this study will be reported later. In this respect, WSFD becomes an useful analogue of the highly efficient and widely used concrete additive, “silica fume ”.

4. Conclusions

WSFDs consist of microporous clusters of spherical particles of Fe oxides. The size of the particles ranges from 10–100 nm.

ZnO content in WSFD strongly affects the hydration of WSFD + cements mixtures, which manifests itself in the time of mixture hardening and the rate of its strength development.

WSFD resemble in its properties very fine silicon flue dusts.

WSFD + cement mixtures show long-term stability and low heavy metals leaching even at WSFD content of 70–80 wt.%

The results of this study are promising both from the standpoint of WSFD solidification and its disposal and the use of these waste materials as novel additives to building materials (concretes).

Acknowledgements

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