

Hardening and properties of cement-based materials incorporating heavy metal oxides

V ŽIVICA

Institute of Construction and Architecture of the Slovak Academy of Sciences, Bratislava, Slovak Republic

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Abstract. The subject of the study was the influence of oxides PbO, ZrO₂ and Cr₂O₃ immobilized in cement matrix. The obtained results show the positive effect of the present oxides in hydrating cement on compressive strength development and the quality of the forming pore structure of the resulting material.

A surprising effect showing the paralysis of the positive effect of heavy metal oxide admixture has been shown by the increasing of the added quantity of PbO (from 1 to 4%) and the used w/c ratio (0.7 instead of 0.4). The increase of the quantity overcoming the optimum of the reaction product of the interaction between hydrating cement and PbO added for the cause of the paralysis is supposed. The explanation of the adverse effect and the identification of the reaction product in question needs more detailed study.

Keywords. Heavy metal oxides; cement matrix; immobilization.

1. Introduction

Solidification and stabilization in cement systems is one from the possibilities of measures aiming at minimizing the environmental risk associated with handling of hazardous wastes. Solidification with cements offers three major advantages: (i) the technology involved in the fabrication of the waste form is simple and available; (ii) a series of studies throughout the world has verified the availability of properties of tailored cementitious formulations and (iii) perhaps most importantly, there is a potential advantage of near-thermodynamic stability offered by a hydrated encapsulant host material. With the exception of the simple four-coordinated oxides of Si, Ti, U and Th, all potential host phases are hydrated at the normally surrounding conditions of temperature and pressure forming thermodynamically stable form (Roy 1982).

Among the different types of wastes one can distinguish between: (i) wastes containing significant quantities of intractable inorganic elements, such as heavy metal oxides like cadmium, mercury, arsenic, selenium, lead, zinc and copper, (ii) radioactive wastes and (iii) wastes containing significant quantities of toxic, hazardous or polluting organic compounds, which cannot be re-processed or recycled utilizing current technologies.

A major point of concern refers to the long-term behaviour of the resulting waste-cement composed products. In this connection it is important to classify the effect of interfering compounds on the hydration of Portland cement (Takashi *et al* 1977). A special attention to the immobilization of heavy metals is paid. These can occur even as radioactive wastes.

The use of Portland cement and its blended species for this purpose is well documented (Gilliam *et al* 1986). The successful immobilization of heavy metals such as Cr, Pb, Ba, Hg, Cd and Zn in cement systems is generally attributed to adsorption

and precipitation of hydroxide phases. In general, transition element compounds, added in cement strongly affect the hydration process. The compounds, e.g. such as PbO and ZnO delay setting and hardening (Barth *et al* 1990; Arliquie *et al* 1983). An exception represents Cr compounds accelerating hardening (Fierens and Verhaegen 1972).

An interesting topic represents the influence of present heavy metal oxides on electrochemical behaviour of embedded steel reinforcement. According to the information given in some papers and our results, oxides ZnO, CuO and PbO represent effective inhibitors of chloride-induced corrosion of concrete steel reinforcement (Tashiro 1984; Tashiro *et al* 1985). On the contrary Cr₂O₃ and MnO act as corrosion-stimulating compounds. According to our results the oxides Cr₂O₃, Fe₂O₃, V₂O₅, CdO, TiO₂ and MoO₃ have been shown as strong corrosion-stimulating substances (Živica and Vargová 1995; Živica and Janotka 1996). Exceptionally strong stimulating is WO₃, causing the total dissolution of steel (Živica 1994).

This study involves series of experiments concerning the influence of heavy metal compounds on hydration and hardening of cement-based materials.

The subject of the paper is the influence of admixture of some heavy metal oxides on the long-term properties of cement based materials.

2. Experimental

The information on the experimental work is given in table 1.

3. Results and discussion

Figures 1 and 2 show the values of compressive strength of the mortars with metal oxide admixtures (MeO_x mortars). The presented values are expressed by the percentage of compressive strength of mortars without MeO_x admixture (plain mortars).

Table 1. Experimental conditions

Test specimens composition	Mortar with cement: sand is in the ratio of 1:3, w/c 0.5 and 0.7, 1 and 4% PbO, ZrO ₂ and Cr ₂ O ₃ admixture from the mass of cement, control mortar without metal oxide admixtures
Curing	3 days at 95% RH and 20°C in moulds (moist curing), after demoulding at RH of 50% and 20°C (air curing). Owing to the delayed hardening of the PbO mortars their moist curing has been prolonged to 10 (1% PbO, w/c 0.5), 14 (1% PbO, w/c 0.7) and 30 days (4% PbO, w/c 0.5 and 0.7)
Test specimens size	20 mm edge cubes
Materials used	Portland cement CEM I 42.5 according to STN PENV 197-1 (table 2), silica sand according to STN 72 1208, commercially available oxides PbO, ZrO ₂ and Cr ₂ O ₃
Properties studied	Setting of the cement pastes with w/c 0.3 and 0.45 and addition of 1.0 and 4.0% PbO, according to STN 72 2115. Bulk weight, compressive strength, total porosity calculated from specific and bulk weights, pore structure (mercury porosimetry mod. 2000 and macroporosimeter 120 Carlo Erba), composition (diffractograph Philips and DTA), bound water and calcium hydroxide contents (thermogravimetrically). For DTA and GTA equipment of MOM Budapest was used.

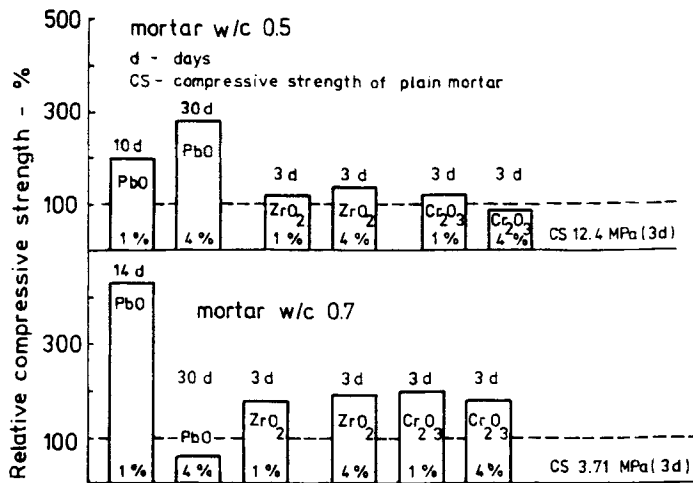


Figure 1. Compressive strength of the mortars after their moist curing.

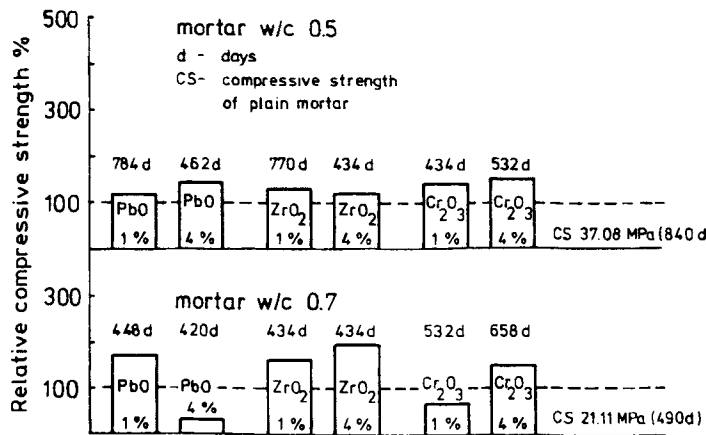


Figure 2. Compressive strength of the mortars after their air curing.

Figure 1 shows that PbO, ZrO₂ and Cr₂O₃ as admixtures accelerated the hardening of the mortars. This effect by the accelerated development of compressive strength of the related mortars has been shown. This accelerating effect by the increased w/c value was expressed.

According to figure 1 the accelerating effect was especially expressed in PbO admixture. Evidently, the efficiency of this admixture positively influenced the prolonged moist curing of the PbO mortars (table 1). This has been caused by the slowing-down of setting of the mortars. It can be supposed that the real accelerating effect of the PbO admixture is not so expressive as shown in figure 1. But, in any case, it can be considered as equivalent to the accelerating effect generated by the ZrO₂ and Cr₂O₃ admixtures. This assumption is confirmed by the comparable long-term values of compressive strength of the MeO_x mortars (figure 2). The slowing-down of the cement pastes caused by PbO admixture is well demonstrated (table 3). Again the adverse effect of PbO admixture, depending on w/c ratio value used can be seen.

Table 2. The properties of used Portland cement.

Composition (%)								
Ignition loss	Insoluble residue	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Total
1.07	1.29	20.57	5.84	3.06	64.42	1.50	2.15	99.9
Setting	begin end		3 h 30 min 5 h		Specific weight kg.m ⁻³ 3 104		Specific surface m ² .kg ⁻¹ 338 (Blaine)	
Mineralogical composition according to Bogue %		C ₃ S 55.66	C ₂ S 17.13	C ₃ A 10.30	C ₄ AF 9.30	CaSO ₄ 3.65		

Table 3. Setting of the cement pastes with the added PbO admixture.

Admixture of PbO (%)	w/c 0.30				w/c 0.45			
	Begin	End	Time	Compressive strength (MPa)	Begin	End	Time	Compressive strength (MPa)
0	3h 40min	5h 40min	2h	29.9	6h 16min	> 21h	> 15h	13.7
1	7h	25h 15min	18h 15min	4.1	—	—	27h	0.6
4	7h	27h 15min	20 h	0.4	—	—	81h	0.2

Table 4. Characteristics of the mortars after their moist curing.

w/c	Added metal oxide (%)	Time of moist curing (days)	Bulk weight (kg.m ⁻³)	Total porosity (%)	Pore median (nm)	H ₂ O bound contents (%)	Ca(OH) ₂ contents (%)	
0.5	PbO	1	10	2114	20.0	192	2.13	0.63
	ZrO ₂	1	3	2139	19.7	531	1.34	2.27
		4	3	2156	18.8	274	1.50	2.23
	Cr ₂ O ₃	1	3	2100	21.4	291	1.62	1.41
		4	3	2120	20.1	431	1.38	1.28
	plain mortar		3	2133	19.6	343	1.35	1.08
0.7	PbO	1	14	2035	22.1	312	1.84	2.99
	ZrO ₂	1	3	2035	23.9	834	1.38	2.44
		4	3	1999	25.0	687	1.42	1.92
	Cr ₂ O ₃	1	3	2012	24.2	789	1.44	1.60
		4	3	2021	23.9	775	1.15	1.80
	plain mortar		3	1990	25.5	967	1.30	2.02

An exception represents the 4% PbO mortar with w/c 0.7 differing by relatively lowest short- and long-term values of compressive strength (figures 1 and 2). It shows the disturbing effect of the hardening in the given PbO mortar. It is interesting that this adverse effect was evoked by the simple increasing by 40% of w/c value used.

Table 5. Characteristic of the mortar after their air curing.

w/c	Added metal oxide (%)	Time of curing (days)	Bulk weight (kg.m ⁻³)	Total porosity (%)	Pore median (nm)	H ₂ O bound contents (%)	Ca(OH) ₂ contents (%)
0.5	PbO 1	784	2206	17.1	152	1.57	4.52
	ZrO ₂ 1	770	2217	17.0	388	2.10	5.85
	4	434	2198	17.3	448	1.82	3.88
	Cr ₂ O ₃ 1	434	2192	16.8	414	1.65	4.40
	4	532	2269	14.2	484	1.45	4.74
	plain mortar	840	2231	16.6	476	1.57	5.85
	PbO 1	448	2177	17.7	479	2.68	6.89
0.7	ZrO ₂ 1	434	2158	18.2	982	2.09	6.05
	4	434	2088	20.4	611	2.11	5.68
	Cr ₂ O ₃ 1	532	2215	16.1	776	2.32	5.71
	4	658	2187	16.8	601	2.25	5.75
	plain mortar	490	2122	20.5	1082	2.05	5.98

Table 6. Characteristics of the PbO mortars.

w/c	Added metal oxide (%)	Time of hardening (days) (MC-Most curing)	Bulk weight (kg.m ⁻³)	Total porosity (%)	Pore median (nm)	H ₂ O bounds (%)	Ca(OH) ₂ contents (%)	Compressive strength (MPa)
0.5	PbO 4	30 MC	2142	18.5	112	2.66	1.15	34.7
0.7		30 MC	1956	27.4	828	1.13	0.26	2.2
0.5	PbO 4	462	2281	13.9	168	2.08	5.02	44.5
0.7		420	2037	17.1	1699	2.30	3.61	6.3

Comparing the values characterizing the pore structure (bulk weight, total porosity, pore median) and cement hydration degree in the mortars (water bound and calcium hydroxide contents), given in tables 4, 5 and 6, the significant differences can be seen in the values of the 4% PbO mortar with w/c 0.7 and those of other studied MeO_x mortars.

As can be seen this mortar is significantly marked off not only by the decreased compressive strength values, but also by the decreased values of bulk weight, calcium hydroxide contents and water bound contents (after moist curing) and by the increased values of total porosity and pore median. In the case of this parameter the difference was especially expressive.

It is known that compressive strength is dependent on the quality of pore structure of the cement-based materials. This quality is moreover dependent on the kind and quantity of the constituents forming pore structure, as cement hydration products and their reaction products with admixtures. Therefore, the cause of the mentioned paralysis of the PbO acceleration effect should be searched in the given pore structure and its constituents. From this viewpoint the reaction products of cement

hydration and MeO_x admixtures in pore structure in the mortars are interesting. Unfortunately, the used DTA and XRD methods for the study of the reaction products have been shown as fully unsuccessful. Evidently the reaction products in question were amorphous or near-amorphous substances and therefore the used methods were unable to identify them. Moreover, the presence of numerical spacings of β -quartz on the XRD-patterns represents a potential factor for superimposing of the spacings of other present substances in the mortars disturbing their identification.

But the found changes in the degree of the pore structure and cement hydration, under the application of MeO_x admixtures, demonstrate the interaction between hydrating cement components and the added MeO_x admixtures. The results of this interaction were undoubtedly the common products. Therefore the anticipation of their existence in the MeO_x mortars is fully entitled. According to this, PbO , ZrO_2 and Cr_2O_3 added to cement seem to be active partners of cement hydration process.

The formation of heavy metal hydroxides of various solubility, or complex compounds and double salts under the presence of heavy metal oxides in hydrating cement is supposed (Chado *et al* 1967; Poon *et al* 1985; Coté 1986). The coating of hydrating particles of cement by these compounds is considered for the cause of the disturbing of cement hardening in some cases.

The formation of large hexagonal crystals of $\text{Ca}(\text{OH})_2$ due to the presence of some heavy metal oxides, resulting in more porous structure of cement matrix seems to be an undesirable factor occurring due to presence of heavy metal oxides (Tashiro *et al* 1985).

Some heavy metal ions, including Pb^{2+} ion, are able to replace part of Ca^{2+} ions in calcium silicate hydrates leading to their amorphization (Komarneni *et al* 1988). It is well known that these hydrates play dominant role in cement-based materials. Therefore, it can be accepted that the effects of the mentioned replacement has an important influence on the properties of cement-based materials, containing heavy metal oxides.

It is evident that interaction of heavy metal oxides and hydrating cement represents a very complex topic.

Undoubtedly for the behaviour of heavy metal oxide admixtures and their influence on hydration and hardening of cement the chemical properties of heavy metal oxides represent the factor of the first order (Remy 1961). For the studied oxides the following characteristics are probably significant for their effects in question: (i) ability of ZrO_2 in strong medium to formate anion $[\text{ZrO}_3^{2-}]$ and on it, based salts containing amorphous hydrated ZrO_2 . This is able to bind the basic compounds, maybe $\text{Ca}(\text{OH})_2$, (ii) Cr^{3+} ion present in Cr_2O_3 has strong tendency to formate complex compounds, Cr^{3+} ion with the strong bases is able to formate hydroxochromic compounds and (iii) Pb^{2+} ion formates with the strong bases of lead hydroxo compounds.

It can be supposed that the mentioned characteristics take place in the interaction of PbO , ZrO_2 and Cr_2O_3 with hydrating cement and the found effects.

According to the obtained results, the formation of the mentioned species (i,ii,iii) and their existence in the mortars probably were favourable as has been shown by the development of short-term compressive strength and their long-term stability. This positive effect of PbO , ZrO_2 and Cr_2O_3 admixture on other engineering properties of cement-based materials can be supposed. Moreover the positive effect seems to be independent of w/c ratio value used. It is important under suitable circumstances from a practical viewpoint.

An exception demonstrating as a paralysis of accelerating effect by PbO admixture under the increasing of w/c ratio value shows the complexity of the interaction. The changed conditions of hydrolysis or the increasing of the quantity of the formed reaction product, overstepping the optimum, seem to be as a potential possibility of the paralysis.

4. Conclusion

- (I) The obtained results show that immobilized PbO, ZrO₂ and Cr₂O₃ in cement matrix positively influence its engineering properties and their long term stability. An interesting and important information is the possibility of the paralysis of the positive effect of the immobilized PbO when the w/c used is increased.
- (II) The found strengthening and strength-degradation effects under heavy metal oxides immobilization in cement matrix are worthy of a more detailed study.

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