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Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement

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Abstract

A fractional factorial design (2^{4-1}) of experiments was carried out to study the influence of metal oxides on cement properties: unconfined compressive strength (UCS), setting time (ST), bulk density (BD) and noncombined water (NCW). Four metal oxides, usually contained in inorganic wastes from thermal processes, were studied: ZnO, Cr_2O_3, PbO, and Fe_2O_3. The amount of these metal oxides in the formulations was selected according to the composition of inorganic wastes from thermal processes: 0–30% dry wt. for Fe_2O_3, 0–15% dry wt. for ZnO, and 0–2.5% dry wt. for PbO and Cr_2O_3. The analysis of the experimental results shows that ZnO retards strongly the ST with respect to that of the cement; it also decreases the UCS of the final product at short ages, but its effect decreases with the sample age. Fe_2O_3 does not affect the ST and UCS at short sample ages; however, at long sample ages, it decreases the UCS of the product. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Metal oxides; Portland cement; Waste management; Compressive strength; Setting time

1. Introduction

Industrial wastes from thermal processes usually contain metal oxides as main constituents. Zinc, iron and lead oxides are found in dusts and sludges recovered after gas treatment in steel factories and foundries, which use scrap as raw material. Chromium oxide is also contained in dust from stainless steel manufacture.

These wastes are usually treated before disposal by means of solidification/stabilisation techniques, using cementitious materials; the potential of reusing these wastes in construction materials is less studied, but some examples can be found in the literature [1].

In this work, four metal oxides, iron (III), zinc, lead and chromium (III) oxides, have been selected to study the setting and hardening behaviour of cement/metal oxides. Several authors have reported the interactions of many inorganic compounds on the setting and mechanical properties of cement-based systems. A literature review about these interactions has been published by Trussell and Spence [2] and Mattus and Mattus [3]; they include the discussion of the qualitative effect of zinc, lead and chromium on the cement properties.

The effect of zinc has been studied by different authors. Arliguie and Grandet [4,5] report that an amorphous layer of $Zn(OH)_2$ is formed during the hydration of C_3S phase in the presence of Zn, thus retarding the hydration of this phase. The hydration of C_3A phase in the presence of Zn is influenced by the amount of sulfate in the cement. When the concentration of sulfate is higher than 2.5%, the hydration of C_3A is retarded. Cullinane et al. [6] and Ortego et al. [7] have studied the effect of zinc nitrate on the cement properties. Cullinane et al. [6] report that the addition of zinc nitrate below 2 wt.% does not modify the UCS values with respect to those of the control mix; however, for higher contents (5% and 8%), the UCS is significantly reduced. Similar observations have been reported by Tashiro et al. [8] who use ZnO instead of $Zn(NO_3)_2$. He postulates that zinc forms an amorphous layer of gel on cement grains.

Tashiro and Oba [9] report that the hydration of C_3A phase is partially hindered in the presence of ZnO; when the substitution is 20 mol% ZnO, a very small amount of hydrate is formed, even after 28 days of curing. The retardation of the early hydration of C_3A is also confirmed by differential calorimetry. The UCS of hardened C_3A is not affected in the presence of 20 mol% ZnO up to 28 days.

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Hamilton and Sammes [1] analyse by X-ray diffraction cement doped with ZnO (1% to 20%). When 10% of ZnO is used, a calcium zinc hydrate is detected after 28 days of curing:

$$2ZnO + Ca(OH)_2 + 4H_2O \rightarrow Ca[Zn(OH)_3H_2O]_2.$$

This compound seems to form a protective layer that inhibits the normal hydration of cement grains. Mollah et al. [10], using FTIR, also suggest a formation of a surface layer of $CaZn_2(OH)_6 \cdot 2H_2O$, which does not allow the transport of water to C_3S phase.

Hamilton and Sammes [1] also investigate the effect of 1% and 5% ZnO on the UCS value of hardened cement. The formulation containing 1% ZnO increases slightly the UCS with respect to cement; however, that containing 5% ZnO decreases the UCS at 3 and 7 days; at 28 days the strength is similar to cement.

Ortego et al. [11] studied the effect of zinc nitrate on the hydration of cement; they observed that 60% of the added water is lost after the exposition of the product in open containers. They indicate that most of the added water does not react with the clinker to form hydration products.

The effect of lead on the hydration of cement phases has also been widely studied. Lead retards the setting of cement, due to the formation of compounds, which cover the silicate phases [7]. Cullinane et al. [6] studied the effect of the additions of PbO on the UCS of cement and found small changes of UCS with respect to the control sample; a maximum increase of 18% is obtained for the sample containing 5% lead as nitrate.

Tashiro and Oba [9] report that common hydration products are formed during the hydration of C_3A in the presence of PbO. However, it decreases the compressive strength of C_3A by a considerable extent. The DSC analysis shows that PbO retards the hydration immediately after pouring water, but is accelerated a few minutes later. Tashiro et al. [8] in a similar study report that ettringite is not formed in the presence of PbO.

Using X-ray diffraction, Hamilton and Sammes [1] do not identify any lead compounds in cement/lead oxide formulations after a 28-day curing period; thus, they conclude that lead compounds in cement matrices are amorphous. They detect portlandite, which is to be expected in cement hydration. These results are in good agreement with the UCS values, wherein slight differences are observed with respect to the control sample.

Ortego [12] suggests that lead is present as sulfate or hydrosulfate species; this fact can be related to the absence of ettringite reported by Tashiro et al. [8].

Zivica [13] studies the long-term behaviour of cement mortars containing PbO and Cr_2O_3 under the action of an NaCl solution. He observes a greater degradation of the mortar compared to the control sample. However, the author reports that these metal oxides can act as inhibitors of chloride-induced corrosion of concrete steel reinforcement. In a later work, Zivica [14] finds an effect of PbO on the hardening of cement-based products depending on the water-to-cement ratio. A water-to-cement ratio in the mortar of 0.7 decreases strongly the UCS value with respect to 0.5.

More recently, Ilic et al. [15] studied the effects of dissolved lead on cement/fly ash systems. They measured the flexural strength of products at 56 days under different conditions and they did not find any important difference with respect to cement/fly ash systems.

Several workers have also studied the influence of chromium compounds on the hydration and hardening of cement-based products. Tashiro and Oba [9] studied the influence of Cr_2O_3 on the hydration and the compressive strength of the hydrated C_3A phase; pastes containing 1 to 5 mol% Cr_2O_3 showed a similar formation of C_3AH_6 compared to pastes without additions of any metal oxides; at higher chromium oxide additions, the hydrate is clearly distinguished at 28 days. With respect to the UCS, the values of the hardened pastes containing 20 mol% Cr were slightly higher than pastes without any addition of metal oxides. Cr_2O_3 retards the early hydration of C_3A, but to a smaller extent than other metal oxides, such as zinc and copper oxides. In a similar work, Tashiro et al. [8] report the effect of Cr_2O_3 on the formation of ettringite; this oxide improves the crystal growth of ettringite, but it reduces the strength of hardened ettringite.

The lower effect of Cr_2O_3 on the setting time (ST) and strength development of cement can be associated with the incorporation of Cr throughout the cement matrix [12].

Mollah et al. [16] studied the incorporation of chromium nitrate in Portland cement type V and IP. EDS and FTIR investigations indicate that chromium compounds are not formed on the surface of hardened cement; these compounds are dispersed below the surface of the OPC matrix. Chromium ions can substitute the silicon in the C-S-H.

The aim of the present paper is to show quantitative correlations of the initial and final setting time (IST and FST), unconfined compressive strength (UCS), bulk density (BD) and noncombined water (NCW) of Portland cement in the presence of several metal oxides. General trends of the variables have been previously established in the literature, but quantitative relationships are necessary in order to estimate the influence of the amount of metal oxides on these properties.

2. Experimental method and results

2.1. Materials

Reagent grade metal oxides were used: Fe_2O_3 from Panreac, and ZnO, PbO and Cr_2O_3 from Aldrich. The particle size was always less than 150 μm. Commercial Portland cement (CEM I, 42.5 R according to UNE 80301-96) was used in the cement/metal oxides products. It was provided by ALFA cements and its composition is shown in Table 1.

Table 1
Oxide composition of Portland cement (%, dry wt.)

Oxide	%, dry wt.
CaO	64.1
SiO_2	20.1
Al_2O_3	6.10
SO_3	3.68
Fe_2O_3	2.20
K_2O	1.48
MgO	1.37
TiO_2	0.33
Na_2O	0.22
SrO	0.12
Total	99.70

Table 3
$2^{4-1}+2$ experimental design

Experimental order	Code	% Fe_2O_3	% ZnO	% PbO	% Cr_2O_3	% Cement
1	S1	15	7.5	1.25	1.25	75
2	S9	30	15	2.5	0	52.5
3	S6	0	0	2.5	0	97.5
4	S7	30	0	2.5	2.5	65
5	S4	0	15	0	0	85
6	S2	0	0	0	2.5	97.5
7	S8	0	15	2.5	2.5	80
8	S5	30	15	0	2.5	52.5
9	S3	30	0	0	0	70
10	S10	15	7.5	1.25	1.25	75

2.2. Experimental design

A fractional factorial design of experiments (2^{4-1}) was performed to evaluate the influence of PbO, ZnO, Cr_2O_3 and Fe_2O_3 on the cement properties: ST, BD, NCW and UCS. Two central points were also performed to calculate the experimental error, and a control mix of cement was included as a reference. In order to obtain products where only one metal oxide was included in the formulation (see Products S6, S4, S2, S3 in Table 3), the minimum values of the experimental design were selected as zero, and the negative generator of the design ($D = -ABC$) was used.

The minimum and maximum values of the four metal oxides (expressed as % in dry product) and the overall design are shown in Tables 2 and 3, respectively. The water content was fixed in all formulations: water-to-solid ratio = 0.366. The order of the experiments was fully randomized, thus providing protection against the effects of lurking variables.

2.3. Mixing procedure

The synthetic metal oxides were previously mixed with Portland cement in a separate vessel; then, mixing was performed according to ASTM C305 mixing procedure for cement pastes, but increasing the mixing time to 2 + 3 min instead of 1 + 2 min, using a sample batch of 2000 g dry wt.

The paste was poured in 50-mm cubic metallic moulds for UCS measurement and in plastic moulds for ST measurement. After sample setting, the cubic samples were demoulded and entered into hermetic plastic bags for curing at room temperature.

Table 2
Experimental design variables

Variables	(%, dry wt in product)		
	Minimum (− 1)	Central (0)	Maximum (+ 1)
A: % Fe_2O_3	0	15	30
B: % ZnO	0	7.5	15
C: % PbO	0	1.25	2.5
D: % Cr_2O_3	0	1.25	2.5
Water-to-solid ratio		0.366	
% Portland cement		balance	

2.4. Measurement of properties

The measurement of ST was performed according to ASTM C191; due to the retardation of setting in some formulations, three plastic moulds were cast in the same batch, in order to use them in a consecutive way in the ST automatic machine (CONTROLS Vicamatic 63-L27/AZ), each mould works for a maximum of 9 h, thus allowing the recording of IST and FST values up to 27 h. For higher values, additional batches were required. Results are shown in Table 4.

The UCS of hardened cement/metal oxides products was performed in triplicate at 1 (or 3), 7, 28, 56 and 90 days, according to ASTM C109. Some products did not set after 1 day; the UCS value was then measured at 3 days. Results are also shown in Table 4.

The BD of products was measured at 56 days after weighting the cubic samples. NCW was also determined at 56 days after drying the samples at 60°C.

3. Discussion

3.1. Calculation of significant effects

In the experimental design, two experiments in the central point were performed. The experiments ($2^{4-1}+2$) allowed the calculation of the average, 4 main factors and 3 two-factor interactions. There were two degrees of freedom to estimate the experimental error of the effects.

The ANOVA test was used to determine the statistical significance of each effect by comparing the mean square of each effect against the estimate of the experimental error, considering two degrees of freedom and 95% confidence level. This method allowed the determination of the significant effects at 95% confidence level.

Table 4
Experimental results: IST and FST, UCS at 1, 3, 7, 28, 56 and 90 days, BD at 56 days and NCW at 56 days

	ST (min)		NCW (%)	Density (g/cm^3)	UCS (MPa)					
Experiment code	IST	FST	NCW$_{56}$	D_{56}	UCS$_1$	UCS$_3$	UCS$_7$	UCS$_{28}$	UCS$_{56}$	UCS$_{90}$
Control	180	495	13.02 ± 0.04	1.992 ± 0.012	35.3 ± 1.0	46.0 ± 1.9	52.9 ± 5.2	55.8 ± 1.3	60.0 ± 8.1	68.0 ± 5.7
S1	3540	3850	12.86 ± 0.02	2.044 ± 0.005	–	0.31 ± 0.12	26.5 ± 1.5	49.2 ± 5.1	51.7 ± 2.9	47.1 ± 2.2
S3	270	450	14.41 ± 0.07	2.062 ± 0.004	28.0 ± 1.7	–	40.2 ± 4.3	45.6 ± 7.3	47.2 ± 6.2	52.8 ± 3.5
S5	7400	10500	10.95 ± 0.09	2.059 ± 0.011	–	–	0.29 ± 0.02	13.9 ± 1.9	34.6 ± 1.1	32.7 ± 3.8
S6	2860	3600	11.83 ± 0.16	1.990 ± 0.010	–	13.8 ± 1.1	41.8 ± 2.6	53.4 ± 11.8	59.2 ± 6.6	61.8 ± 5.5
S8	5312	5750	13.12 ± 0.23	2.038 ± 0.004	–	–	13.5 ± 0.6	43.4 ± 6.1	55.1 ± 7.4	53.9 ± 8.1
S7	2320	2800	13.60 ± 0.23	2.076 ± 0.010	–	30.8 ± 1.7	37.2 ± 4.0	44.4 ± 3.9	41.6 ± 4.3	53.9 ± 6.0
S9	3000	4288	16.09 ± 0.41	2.118 ± 0.005	–	1.19 ± 0.04	13.7 ± 0.4	26.5 ± 2.9	20.2 ± 0.5	24.8 ± 2.6
S4	5650	8000	11.36 ± 0.07	2.019 ± 0.011	–	–	0.16 ± 0.01	44.4 ± 4.0	52.2 ± 6.8	62.1 ± 3.7
S2	290	500	13.40 ± 0.08	2.001 ± 0.004	33.9 ± 1.5	–	52.7 ± 2.9	60.2 ± 1.3	69.6 ± 3.1	67.5 ± 6.2
S10	3280	3700	11.60 ± 0.05	2.055 ± 0.004	–	1.47 ± 0.12	23.7 ± 0.1	46.3 ± 6.0	52.5 ± 8.9	57.1 ± 3.8

3.2. Setting time

From the experimental design, the maximum, minimum and average values of the IST and FST are shown in Table 5 together with the main effects and two-factor interactions. The values are reported as relative values with respect to the ST of the Portland cement, 180 and 495 min for IST and FST, respectively. The significant effects calculated by the procedure described above are in bold characters.

The products containing Cr_2O_3 or Fe_2O_3 as metal oxides have a similar ST to that of cement, however, products containing lead and/or zinc oxides are strongly retarded. The influence of these four metals on the ST can be obtained from the analysis of the factorial design.

From Table 5, it can be observed that four effects are significantly different from zero: B, $AD-BC$, $AC-BD$ and D. ZnO (B) is the most important effect on the IST and FST, increasing the average of the design in 21.70 units. The IST and FST of Product S4, which contains only 15% of ZnO, are 5650 and 8000 min, respectively. The retardation effect of zinc compounds has been widely reported in Refs. [4,5,8–10], assuming a protective layer of zinc compounds on cement grains.

Table 5
ST: average, minimum and maximum values, and main effects and two-factor interactions

	ST (relative to cement)	
	Initial	Final
Portland cement	180 min	495 min
Average	18.85	8.78
Minimum	1.50	0.91
Maximum	41.11	21.21
S.D. in the central point	1.021	0.214
Effect		
A: Fe_2O_3	– 1.56	0.095
B: ZnO	**21.70**	**10.70**
C: PbO	– 0.16	– 1.52
D: Cr_2O_3	**4.92**	1.62
$AB-CD$	– 0.002	0.95
$AC-BD$	– **6.36**	– 2.38
$AD-BC$	**13.00**	**7.02**

The retardation effect of ZnO is enhanced by the presence of other metal oxides; however, the two-factor interactions do not allow the evaluation of these effects separately. The effect of chromium (III) oxide (D) seems to be disturbed by some two-factor interactions, because it increases the average of the design (which is 19 times that of the Portland cement) in 4.92 units. However, the experiment S2, which only contains Cr_2O_3 showed a similar ST compared to the control sample, which is in good agreement with the literature [9,12]. Lead oxide does not affect the average of the design, but it increases strongly the ST with respect to cement.

A linear regression could be used for the evaluation of IST and FST considering the significant effects expressed as % dry wt. in product formulation: B: ZnO; AD: $Fe_2O_3 \cdot Cr_2O_3$; BC: ZnO·PbO; AC: Fe_2O_3·PbO; and D: Cr_2O_3. To solve the confusion among the two-factor interactions, different linear regressions were checked combining the two-factor interactions, and the variables leading to the highest regression coefficient were selected (Eqs. (1) and (2)):

$$\frac{\text{IST (min)}}{180} = 8.30 + 10.84\left(\frac{B}{7.5}\right) - 1.78\left(\frac{D}{1.25}\right) - 2.76\left(\frac{A}{15}\right)\left(\frac{C}{1.25}\right) + 4.24\left(\frac{A}{15}\right)\left(\frac{D}{1.25}\right)$$

$$r^2 = .900 \tag{1}$$

$$\frac{\text{FST (min)}}{495} = 3.42 + 7.48\left(\frac{B}{7.5}\right) - 2.14\left(\frac{B}{7.5}\right)\left(\frac{C}{1.25}\right)$$

$$r^2 = .853 \tag{2}$$

3.3. Unconfined compressive strength

From the experimental design, the maximum, minimum and average values of the UCS of the samples at 7, 28, 56 and 90 days are shown in Table 6 together with the main effects and two-factor interactions. The values are reported as the percentage with respect to the standard value for the Portland cement used in this work, 42.5 MPa at 28 days [17]. The significant effects calculated by the procedure described above are in bold characters. The UCS at 1 and 3 days was not considered in the design as a response variable because of the lack of some values, due to longer ST in some products.

The lowest values of UCS at short and long sample ages are obtained in Products S5 and S9. These are samples containing the maximum amount of ZnO and Fe_2O_3. All products containing 15% ZnO have a very low UCS at 7 days; this fact may be associated to the retardation of the setting. At 28 days, most of the products have a UCS value higher than that of the reference (42.5 MPa).

The influence of these metal oxides on the UCS at 7, 28, 56 and 90 days has been evaluated from the analysis of the factorial design. From Table 6, it can be observed that the most significant effects for UCS at short age (7 days) are *B* (ZnO) and *AD–BC* ($Fe_2O_3 \cdot Cr_2O_3 - ZnO \cdot PbO$), which were also the most significant effects for ST. However, at 28 days, the Fe_2O_3 content has the same effect as ZnO, and at higher sample ages, the effect of Fe_2O_3 increases, decreasing that of ZnO.

The influence of zinc compounds on the UCS of cement–waste systems has been widely reported in the literature; small contents of zinc compounds do not decrease the UCS of cements. Thus, Cullinane et al. [6] report that the UCS of cement is not modified when adding less than 2% of zinc nitrate. Similar behaviour is found by Hamilton and Sammes [1] for 1% ZnO. When the amount of zinc compounds is higher than 5%, a reduction of UCS is observed [1,6]. This is in good agreement with the results of the present work, where the zinc oxide content ranges from 7.5% to 15% in the dry product.

However, the negative effect of iron oxide on the UCS at long sample ages has not been pointed out in the literature. This oxide is usually the main constituent in several industrial wastes and by-products, such as electric arc furnace dust, foundry wastes and slags. Therefore, the content of iron oxide should be considered in case of reutilization of wastes and by-products.

Table 6
UCS at 7, 28, 56 and 90 days relative to cement: average, minimum and maximum values, main effects and two-factor interactions

UCS (%, relative to 42.5 MPa)				
	7 days	28 days	56 days	90 days
Portland cement	124.5	131.3	141.2	160.0
Average	58.8	100.7	113.9	120.9
Minimum	0.37	32.6	47.6	58.4
Maximum	124.1	141.7	163.8	158.7
Effect				
A: Fe_2O_3	– **9.5**	– **41.7**	– **54.3**	– **47.6**
B: ZnO	– **85.0**	– **44.7**	– **32.5**	– **36.7**
C: PbO	7.5	2.5	– 16.0	– 12.15
D: Cr_2O_3	5.0	– 4.2	13.0	3.8
AB–CD	**10.2**	– 13.7	– 7.5	– 21.2
AC–BD	4.5	11.2	– 7.0	4.2
AD–BC	– **24.0**	11.2	– 3.0	6.7

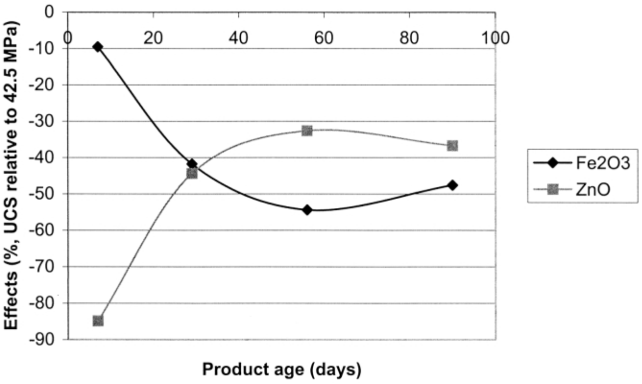

Fig. 1. Evolution of the main effects affecting UCS with sample age.

The evolution of the main effects affecting UCS with sample age can be observed in Fig. 1: the increase of the effect of Fe_2O_3 with product age, and the decrease of that of ZnO, becoming constant after 56 days.

Four linear expressions have been obtained for the estimation of the UCS at 7, 28, 56 and 90 days (Eqs. (3)–(6)):

$$\frac{\mathrm{UCS}_7\ (\mathrm{MPa})}{42.5}100 = 111.3 - 10.09\left(\frac{A}{15}\right) - 55.46\left(\frac{B}{7.5}\right) + 5.14\left(\frac{A}{15}\right)\left(\frac{B}{7.5}\right) + 7.87\left(\frac{B}{7.5}\right)\left(\frac{C}{1.25}\right)$$

$$r^2 = .977 \tag{3}$$

$$\frac{\mathrm{UCS}_{28}\ (\mathrm{MPa})}{42.5}100 = 143.7 - 20.88\left(\frac{A}{15}\right) - 22.21\left(\frac{B}{7.5}\right)$$

$$r^2 = .847 \tag{4}$$

$$\frac{\mathrm{UCS}_{56}\ (\mathrm{MPa})}{42.5}100 = 157.4 - 27.19\left(\frac{A}{15}\right) - 16.33\left(\frac{B}{7.5}\right)$$

$$r^2 = .863 \tag{5}$$

$$\frac{\mathrm{UCS}_{90}\ (\mathrm{MPa})}{42.5}100 = 163.0 - 23.80\left(\frac{A}{15}\right) - 18.37\left(\frac{B}{7.5}\right)$$

$$r^2 = .815 \tag{6}$$

where *A*: Fe_2O_3, *B*: ZnO, *AB*: $Fe_2O_3 \cdot ZnO$, and *BC*: $ZnO \cdot PbO$. *A*, *B* and *C* are expressed as % dry wt. in product formulation.

The evolution of the UCS of cements containing these metal oxides with sample age should follow a trend similar to that corresponding to the average of the design, which is represented in Fig. 2. At early ages, the UCS is reduced because of the retardation effect of metal oxides on the hydration reactions of Portland cement, but after 28 days, the average value overcomes the reference value (42.5 MPa).

The relationship between UCS and product age can be described by a hyperbolic model: (Eqs. (7))

$$\mathrm{UCS(t)}\,\frac{100}{42.5} = \frac{\mathrm{at}}{1+\mathrm{bt}} \quad \text{UCS in MPa} \tag{7}$$

leading to the parameter values, $a = 15.097$ day^{-1} and $b = 0.114$ day^{-1} for the average of the design, and $a = 172.34$ day^{-1} and $b = 1.185$ day^{-1} for the control sample. The *a*/*b* ratio indicates the value of UCS at $t \to \infty$. This ratio is similar for the average and for Portland cement, 132.2% vs. 145.4%, however, the initial rate of hardening, represented by the *a* parameter is much higher than the average for Portland cement.

3.4. BD and NCW

The maximum, minimum and average values of the BD and NCW at 56 days are shown in Table 7 together with the main effects and two-factor interactions. The values are reported as % relative to the hardened Portland cement: 1.992 g/cm^3 and 13.02% wet wt. for BD and NCW, respectively.

From Table 7, a small range of the experimental values of both response variables can be observed; however, the experimental error is lower compared to the ST and UCS measurements. Two effects affect the BD of the hardened product, Fe_2O_3 and ZnO; both oxides represent the highest cement substitutions.

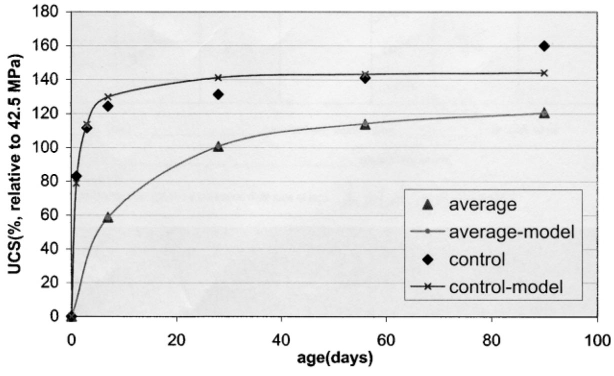

Fig. 2. Evolution of the UCS of cement/metal oxides products with sample age.

Table 7
BD and NCW at 56 days, % relative to cement: average, minimum and maximum values, and main effects and two-factor interactions

	56 days	
	BD	NCW
Portland cement	1.992 g/cm^3	13.02 % wet wt.
Average	103.0	99.7
Minimum	99.9	84.1
Maximum	106.3	123.6
Effect		
A: Fe_2O_3	**3.3**	10.2
B: ZnO	**1.3**	− 3.3
C: PbO	0.97	8.7
D: Cr_2O_3	− 0.17	− 5.0
AB−*CD*	− 0.17	− 0.4
AC−*BD*	0.82	7.9
AD−*BC*	− 0.92	− 17.8

A polynomial expression describes the influence of iron and zinc oxides on the BD of the hardened products at 56 days (Eqs. (8)):

$$\frac{\mathrm{BD}_{56}\ (\mathrm{g/cm^3})}{1.992}100 = 100.4 + 1.66\left(\frac{A}{15}\right) + 0.66\left(\frac{B}{7.5}\right)$$

$$r^2 = .823 \tag{8}$$

where *A* (Fe_2O_3) and *B* (ZnO) are expressed as % dry wt. in product formulation.

None of the effects seem to affect significantly the NCW; therefore, an average value can be considered from the design (Eqs. (9)):

$$\frac{\mathrm{NCW}_{56}\ (\%)}{13.02}100 = 99.7 \pm 3.8 \tag{9}$$

The curvature test was applied to check the linearity of the results in the experimental range of variables [18]; from this test, it was concluded that a linear model could describe the ST, UCS and BD of the studied products.

4. Conclusions

A fractional factorial design of experiments (2^{4-1}), with two central points and one reference point, Portland cement, has been performed to study the influence of iron (III), zinc, chromium (III) and lead oxides on the cement properties: IST and FST, UCS at 7, 28, 56 and 90 days, BD and NCW.

Results lead to the following conclusions.

- ZnO retards strongly the IST and FST with respect to that of cement, and also with respect to the average of the experimental design.
- ZnO decreases the UCS of final product at short sample ages (7 and 28 days), but its effect decreases with the sample age.

- The influence of the sample age on the UCS can be described by a hyperbolic equation.
- Fe_2O_3 does not affect the setting and UCS at short sample ages; however, at long sample ages, it decreases the UCS of the product to a greater extent compared to ZnO.
- Cr_2O_3 does not affect the UCS of cementitious products; only a slight increase of UCS can be observed at 56 days. With respect to the ST, Product S2, which only contains Cr_2O_3 (2.5%) does not retard the setting. However, the overall effect of Cr_2O_3 is significantly important with respect to the average of the design, which means that the interaction of Cr_2O_3 with the other metal oxides retards the setting of the products.
- PbO has a negligible effect on setting with respect to the average, but it retards the setting with respect to cement. It does not affect the UCS of cementitious products at long sample ages.
- The effect of the studied metal oxides on BD and NCW is almost negligible.
- A quantitative evaluation of IST, FST, UCS_7, UCS_{28}, UCS_{56}, UCS_{90} and BD_{56} can be performed by multiple linear models with the obtained parameters in the researched range of variables.

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