Mechanical behaviour of Portland cement mortars with incorporation of Al-containing salt slags

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Abstract

Recovery of a salt cake slag produced from aluminum scrap re-melted in rotary furnaces, at the lowest cost, while complying with all environmental laws is the main objective of this study. The characterisation of the slag residue involved determinations of the water leaching conditions, toxicological analysis, chemical analysis of the leaching waste, and mineralogical composition. A two-phase study was made to determine the effect of waste additions on mechanical properties of cement mortars, involving partial replacements of either sand or cement. SEM characterisation of fracture surfaces was also made. Partial substitution of cement, which is the most expensive component of the mortar, by salt slag has both environmental and economical advantages. However, only small amounts (up to 10 wt.%) can be replaced by washed slag without significant damage to mortar characteristics. Sand substitution by slag is less problematic and 30–50 wt.% replacement levels are easily achieved. However, the direct economical impact is less relevant. The incorporation of unwashed slag in impracticable, as a result of noxious gases released and significant volumetric expansion effects. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Waste management; Mortar; Portland cement; Salt slag; Mechanical properties

1. Introduction

During the recovery of aluminum through scrap recycling, a great quantity of oxide layer forms on the surface of molten metal, which has to be removed from the melt to refine the quality of the final product. In order to promote an easier separation and to avoid the formation of additional oxidation phases, it is common to use a protective salt cover. The molten salt flux promotes the coalescence of suspended metal droplets and helps separate the clean metal from oxide contamination. The scum formed on the surface of molten metal is made of a mixture of oxides, fluxes, gases, and some free metal. Its common name is aluminum salt slag.

Fluxing techniques and production practices strongly change throughout different industries giving several types of dross, normally called white and black. White dross is produced from a melting process of strongly pure scraps, having high aluminum metal content. In this case, fluxing inside the furnace is practically absent and the color of dross skimmed is gray or metallic white. Black dross is produced by secondary aluminum smelters, by using rotary furnaces to melt old casting and a low-grade aluminum scrap. Fluxes are composed of mixtures of sodium and potassium chlorides, and contain small amounts of fluorides. At high molten-metal temperatures, the flux melts and becomes dark. This slag is highly salt-rich (50–70%) and is the object of our study.

The Environmental Protection Agency of the US (EPA) classifies these residues as toxic and hazardous wastes [1]. Even the poorer aluminum-rich residue is very prone to leaching chlorides when in contact with rainfall or groundwater. Moreover, salt slag evolves gases when in contact with water, namely hydrogen, ammonia, methane, and

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small amounts of hydrogen sulfide and phosphine. Some of these gases are explosive, poisonous, and might produce extremely unpleasant odors [2]. The correct disposal of these wastes causes environmental concerns. The treatment of salt cake to minimize land-filling problems is generally done in Europe, US and Canada. Typically, a dry separation process of the aluminum, followed by leaching and filtration steps to separate the soluble flux salts from the insoluble oxides, and crystallization to regenerate the salt fluxes in usable form are the main steps of that treatment. Thus, the waste material is separated into a suitable melted metallic fraction, a reusable salt flux and an inert oxide mainly composed of Al_2O_3 and a spinel which has several possible industrial applications including the construction sector, to improve the mechanical strength of mortar and concrete.

2. Experimental

2.1. Characterisation of the residue

A salt slag from a Portuguese aluminum-alloy producing industry (Alpor, Braga) was used in this work. The adaptability of the residue to the washing by water process was studied first by doing leaching tests in several conditions and by measuring the compositions of the insoluble part and of the solution [3]. The correct sampling of the slag was obtained by following normalised methods

[4]. Grain size distribution of the washed residue was made by sieving and the following result was obtained: >1.40 mm = 11%; 0.5–1.40 mm = 7%; 0.18–0.50 mm = 19%; <0.18 mm = 60%. Chemical composition of each sieved fraction was estimated by X-ray fluorescence (see Table 1). Mineralogical determinations were also obtained by X-ray diffraction.

2.2. Incorporation in cement mortars

These tests are contained in a more embracing study about the economical viability of the development of a correct technology for treatment of salt slag containing insoluble aluminum oxides. In this case, the search for an alternative way to obtain an alumina-rich product that could be economically interesting to be incorporated in construction materials, like in cement mortars, is the central goal of the work.

Mortar preparation was conducted according to the EN196-1 procedure [5]. Two sets of experiments were done, one involving the substitution of sand by the residue and another where cement by slag substitution was promoted. Flexural and compression strengths were measured on prismatic samples, having dimensions of 40 × 40 × 160 mm. These measurements were carried out after curing periods of 3, 7, 28, and 90 days in a standard testing machine (Autograph AG-A, Shimadzu, Japan). According to standard procedures [5], the arithmetic mean of six tests was determined.

Table 1
Chemical analysis (XRF) of different sieved fractions of the washed residue (% or ppm)

| Component | Retained fractions by sieving (mm) | | | | | | | | | |
	1.00	0.71	0.50	0.355	0.25	0.18	0.125	0.09	0.063	<0.063
NaCl	0.9	0.8	0.7	0.8	0.6	0.5	0.3	0.4	0.3	0.3
KCl	2.0	2.3	1.8	1.9	1.4	0.9	0.7	0.5	0.5	0.6
MgO	9.7	9.6	10.0	9.9	10.1	10.2	10.2	10.4	10.4	10.0
Al_2O_3	60.6	62.4	62.2	61.4	60.4	61.8	65.3	70.9	69.7	69.6
SiO_2	8.4	6.6	6.5	5.7	5.8	4.3	4.1	4.3	4.3	4.4
P_2O_5	0.33	0.40	0.35	0.40	0.36	0.40	0.34	0.34	0.34	0.32
S*	1980	2070	1780	1960	1730	1780	1470	1820	1830	1610
CaO	7.1	7.3	7.1	7.0	6.6	5.8	6.3	5.1	5.7	6.0
TiO_2	4.9	6.4	6.6	8.4	10.4	12.1	9.2	4.7	5.2	5.1
V_2O_5*	290	390	470	370	430	440	400	240	290	330
Cr_2O_3*	1590	1220	1790	2370	2150	1500	1410	1240	1310	1180
MnO*	1570	1360	1430	1250	1300	1110	910	890	900	960
Fe_2O_3	2.6	2.8	3.0	2.7	2.6	2.2	2.0	1.9	1.9	2.0
Ni*	170	170	190	250	150	130	190	210	170	240
Cu*	23,800	8100	9500	8300	8300	6300	5700	4700	5100	6000
Zn*	1270	1480	1300	960	910	690	550	490	540	590
Sr*	150	160	160	170	160	130	110	90	100	100
ZrO_2*	460	240	640	690	450	460	490	300	330	370
Sn*	270	350	220	170	150	170	160	150	150	170
BaO*	860	1050	1170	1470	1670	1720	1980	1680	1860	1810
PbO*	1730	2210	2030	2190	2170	2290	2190	2080	2070	2150
Other*	157	142	190	233	99	304	234	200	176	121

  * Results in parts per million (ppm).

The composition of non-slag-containing mortars was also normalised [6] and were obtained by mixing 1350 g of standard sand (silica-rich) with 450 g of cement (Portland type I, class 42.5) and 225 ml of water. Several mixtures containing different weight percentages of previously washed residue were prepared (see Table 2). The high water demand of the slag led to the preparation of mixtures that contain relatively higher amount of water to get enough workability. Different tests involving coarse (up to 2 mm) and fine particle fractions (<180 μm) were made.

The curing process was also conducted in normalised conditions with mortar samples immersed in water and placed inside a humidity-controlled chamber.

3. Discussion of results

As an attempt to define optimal washing conditions, the following laboratory-scale sequence was tested: (i) a sample of milled and dry salt slag was stirred for 1 h in a glass beaker with deionised water corresponding to the solid/liquid ratio of 1:2; (ii) a clear liquid sample was extracted and its density and amount of dissolved salts were determined by pycnometry and evaporation methods, respectively; (iii) these salts were redissolved into deionised water that was added to the slag sample in the beaker to keep constant the solid/liquid ratio (1:3); (iv) steps (ii) and (iii) were repeated for 1:4, 1:5, 1:6, 1:7, and 1:8 solid/liquid ratios. Fig. 1 shows the density evolution of the liquid in contact with salt slag as well as the percentage of salt slag dissolved. Once the 1:5 washing step was reached, almost no more salt slag was dissolved.

To achieve optimal levels of washing efficiency when using cold water, another sequential test was done, starting from a suspension made by the solid/liquid ratio of 1:4. The salt slag was then added to reach final ratios of 3:4 and both liquid density and amount of dissolved salt were determined (Fig. 2).

Leaching treatment was conducted by dissolving 50–60% of the as-received material, which proved to be very effective in the removal of alkaline salts (almost complete). Leached waste is very dark and is mainly
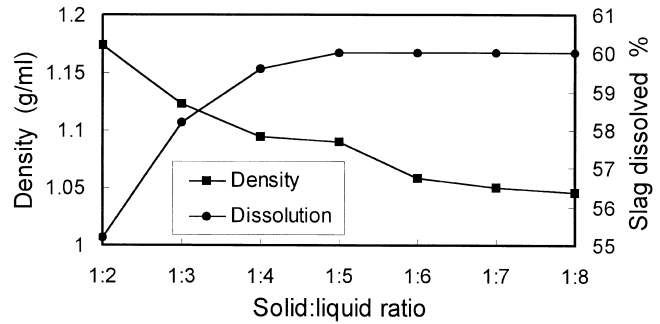

Fig. 1. Dissolution of salt slag having different densities as a function of the water added.

composed of aluminum oxides, hydroxides and silicates, and residual chlorides. Saturated brine contains about 300 g/l of sodium/potassium chlorides and its density is about 1.2. Leaching tests of washed slags allowed their classification as non-toxic materials, while the as-received residues were highly toxic. The inertness character of the treated slag allows its use for different applications [7,8].

Salt slag is initially composed of a heterogeneous mass in which two main mineral groups were found: (i) water-soluble compounds, mainly alkaline salts (NaCl and KCl) but also traces of AlN, AlC_3 and Al_2S_3; (ii) non-soluble compounds in water, mainly corundum (α-Al_2O_3), Al_2S, a spinel of the system MgO–Al_2O_3, quartz, and β-CaO·SiO_2. The main crystalline phases present in the fine fraction are given in Fig. 3. TGA analysis showed that the material is non-reactive above nearly 600°C, while under this temperature, strong decomposition reactions are observed due to the presence of hydroxides and organic matter.

It was found impossible to make cement mortars containing non-washed slags due to the volumetric expansion observed during setting. The chloride content is significant and high concentrations of noxious gases are released.

The dependence of the mechanical resistance of samples as a function of slag amount, the setting time and the average grain size of the residue is shown in Figs. 4–6
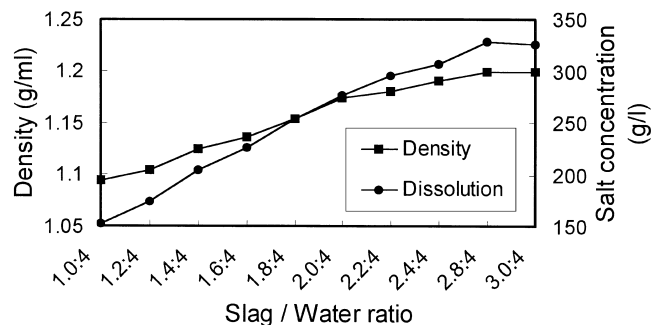
Table 2
Compositions of tested mortars involving slag fractions under 180 μm

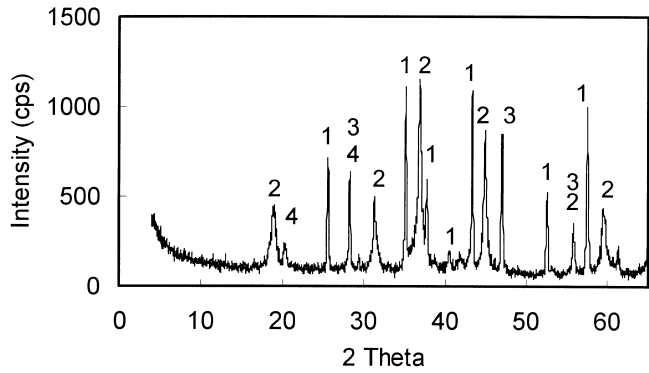| Type of substitution	Percentage slag	Amount of components (g)			
		Sand	Cement	Slag	Water
Sand/slag	0	1350	450	0	225
	10	1305	450	45	225
	20	1260	450	90	230
	30	1215	450	135	250
Cement/slag	10	1350	405	45	225
	30	1350	315	135	225
	50	1350	225	225	250
	70	1350	135	315	260

Fig. 2. Characteristics of the washing solution of the salt slag.

Fig. 3. XRD pattern of the powder fraction under 180 μm. (1) α-Al_2O_3, (2) $MgAl_2O_4$, (3) CaF_2, (4) $Al_2Si_4O_{10}$.

for samples in which residue for sand substitution was promoted. The addition of coarse slag grains promotes deleterious effects on the mechanical properties of the mortars. Samples containing 20% and 30% of slag seem to be weaker than the others (Fig. 4), but the differences tend to decrease for longer curing periods. After 28 days, the resistance of all samples tends to be more similar. This observation is an indication of the retarding action of the sludge, probably due to its acidic nature and incomplete correction of pH.

On the contrary, the addition of small amounts (up to 30 wt.%) of washed fine-grained slag did not decrease the mechanical properties of the mortars (Fig. 5). The good dispersion of these smaller particles through the cement matrix might assure the formation of a suitable micro-structure. Therefore, the slag cannot be considered as a
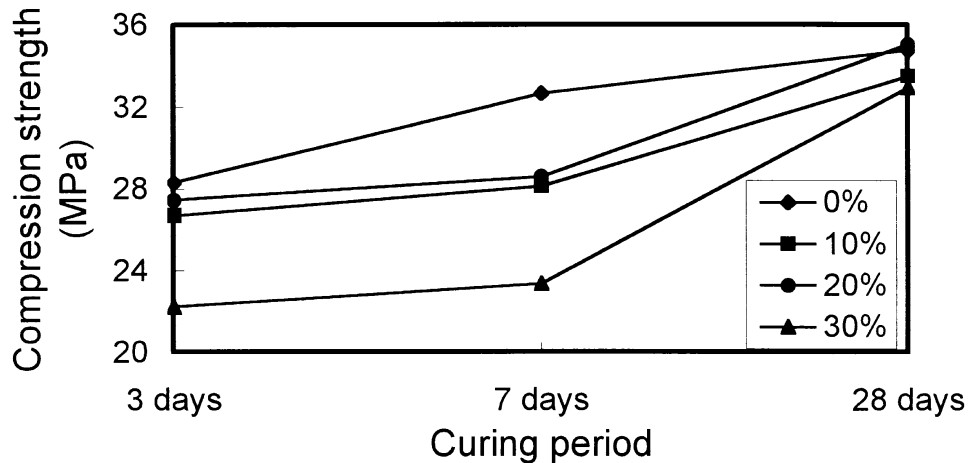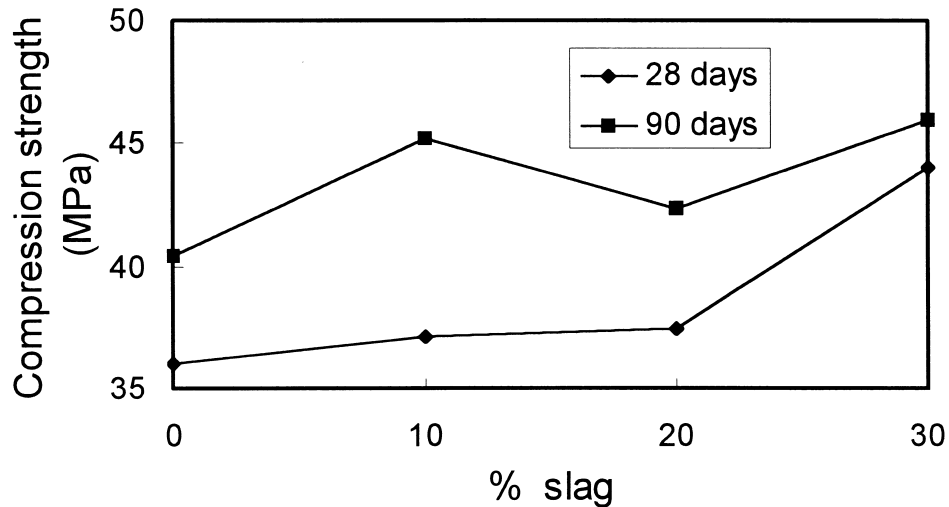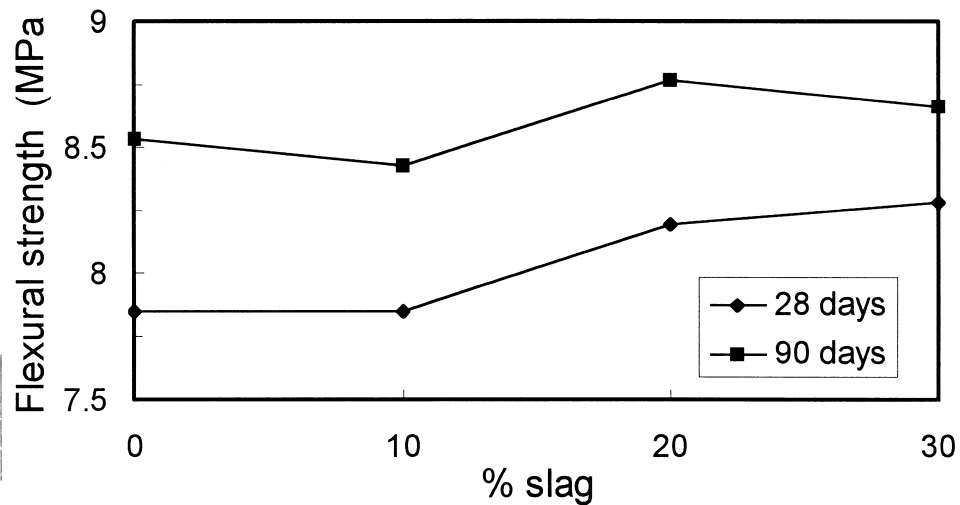

(a)
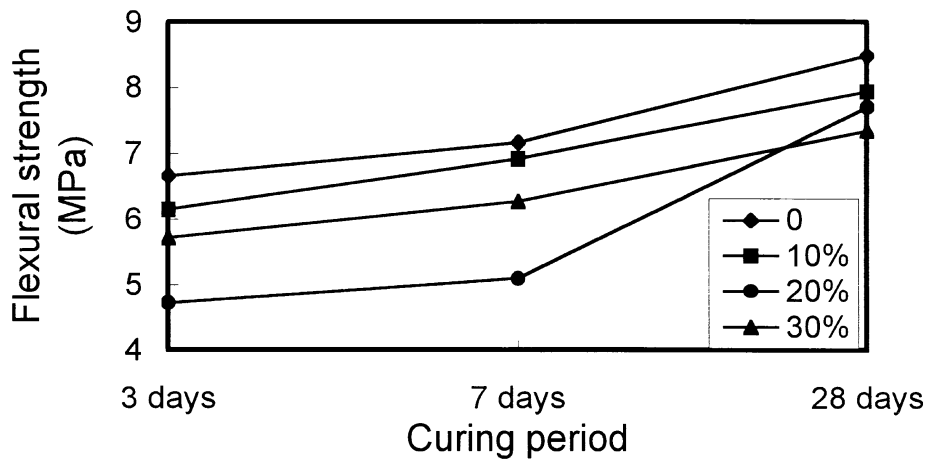
(b)

Fig. 4. Dependence of the mechanical resistance of mortars on the curing period and on added amount of washed coarse salt slag (<2 mm) to partially substitute the sand fraction: (a) compression and (b) flexural strengths.

(a)

(b)

Fig. 5. Dependence of the mechanical resistance of mortars on the curing period and on the added amount of washed fine salt slag (<180 μm) to partially substitute the sand fraction: (a) compression and (b) flexural strengths.

totally inactive additive. Moreover, the previous slag washing treatment is certainly more efficient by using finer particles and ageing effects on the materials properties are less probable.

A direct comparison of samples containing coarse- and fine-grain residue additions is given in Fig. 6. The benefit is much more evident on using fine-grained slag fractions, especially on flexural resistance of the mortars. However, the sieving operation enhances the treatment cost of the

residue, as it requires a previous (and efficient) drying step and the use of grinding facilities to recover the coarser particles.

The typical microstructures (SEM) of fracture surfaces of mortars with or without slag incorporation (partially replacing the sand) are shown in Fig. 7. The changes are less visible, but slag-containing samples seem to be more compact, which is in accordance with improving mechanical characteristics previously discussed.
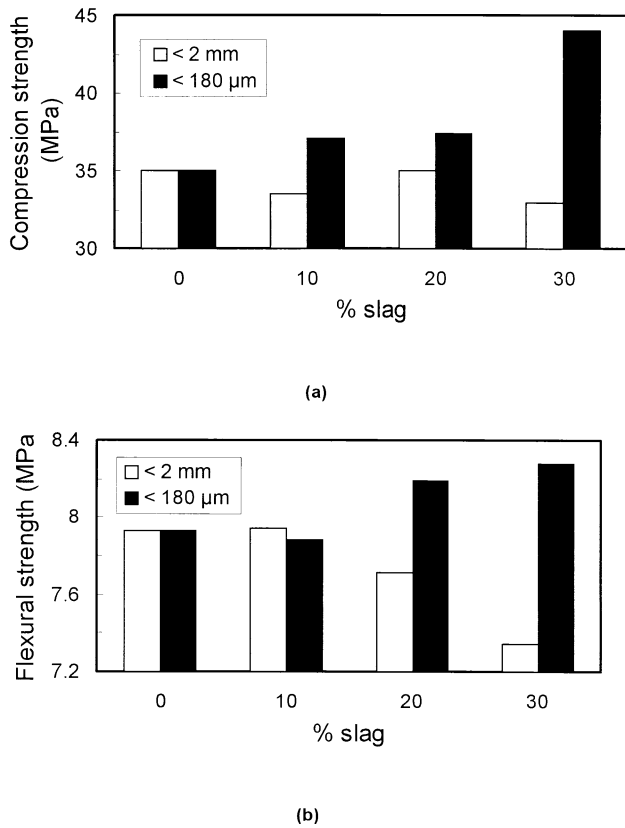
(a)

(b)

Fig. 6. Changes in the mechanical resistance of mortars after curing for 28 days as a function of the amount and average grain size of washed salt slag used to partially replace the sand: (a) compression and (b) flexural strengths.

Fig. 8 shows the mechanical behaviour of samples where cement for slag substitutions were promoted. Both compression and flexural strengths decrease with increasing slag contents, irrespective of the curing period. This deleterious trend was predicted and would also be expected for any kind of cement for inert substitution, whatever the nature of the inert material. In fact, the structural support of these mortars is obviously given by the cement, and its decreasing amount has a negative impact on the mechanical resistance.

The maximum chloride contents for different concrete types are given in Table 3 [9]. The 30% slag-containing mortars, corresponding to the higher and acceptable incorporation limit, were tested and chloride contents (expressed as percentage of the cement) of about 0.4% were determined. This confirms the potential of this incorporation route for non-hazardous slag on mortar fabrication for normal concrete.

4. Conclusions

The incorporation of washed aluminum-containing salt slag in cement mortars seems possible within controlled limits. For samples containing a fixed amount of cement,

the slag for sand substitution (for levels up to 30 wt.%) did not promote deleterious effects on the mechanical properties. At the same time, some properties benefit was found for samples containing fine slag particles (under 180 μm) and especially for longer curing periods (28 or 90 days). Slag for cement substitution on samples containing a fixed amount of sand strongly affects the mechanical properties, and low tolerable levels are accepted (up to 10 wt.%). Even this result might be attractive from an economical point of view, due to the high cost of the cement. At the same time, this replacement seems to be a helpful solution to partly solve the environmental problem associated with the production of such type of slags. The incorporation of salt slag increases the mortar water demand, making this effect more pro-
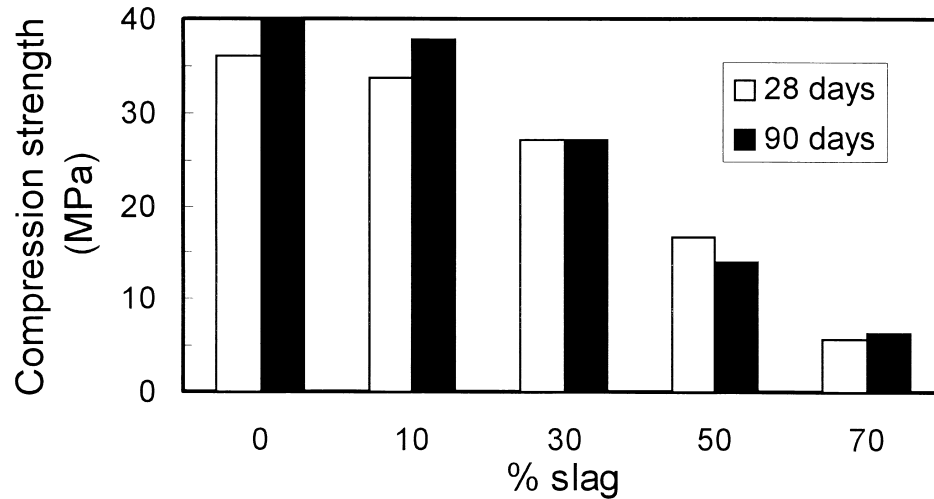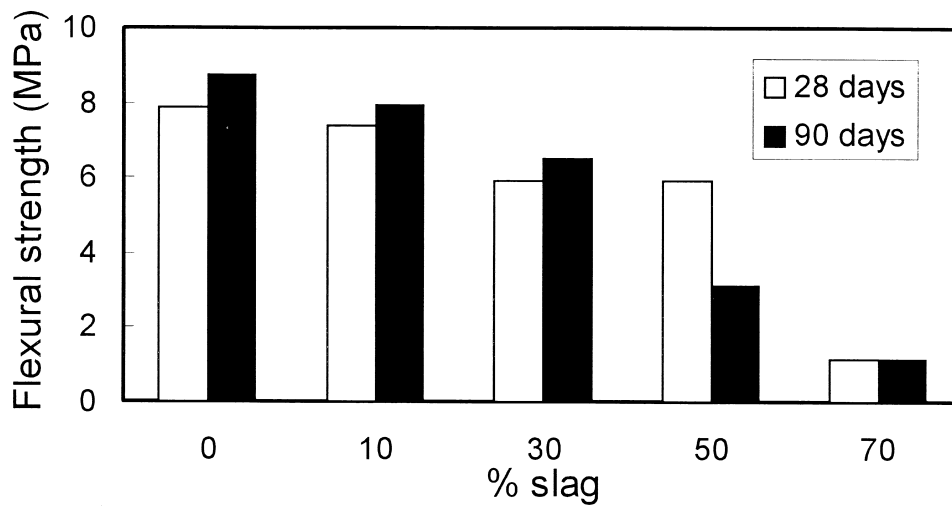

(a)
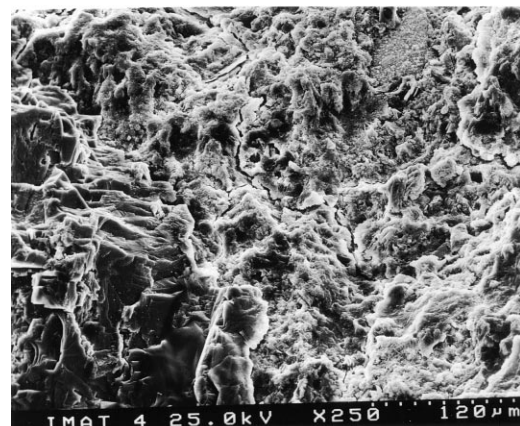
(b)

Fig. 7. Scanning electron micrographs obtained on fracture surfaces of (a) slag-free and (b) 30 wt.% slag-containing mortars.

(a)

(b)

Fig. 8. Dependence of the mechanical resistance of mortars on the curing period and on the added amount of washed fine salt slag (<180 μm) to partially substitute the cement: (a) compression and (b) flexural strengths.

nounced with the use of finer particles and for cement by slag replacing samples.

Table 3
Maximum limits of chloride content in different concrete types

Type of concrete	Cl percentage in cement
Normal	1
Reinforced	0.4
Pre-stressed	0.2

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