Pergamon

Cement and Concrete Research 29 (1999) 171–177

CEMENT AND CONCRETE RESEARCH

Properties of blast-furnace slags containing high amounts of manganese

Jean Péra *, Jean Ambroise, Michel Chabannet

Unité de Recherche Génie Civil-Matériaux, Institut National des Sciences Appliquées de Lyon, 20, Avenue Albert Einstein, 69621 Lyon, France

Manuscript received 10 December 1997; accepted manuscript 6 March 1998

Abstract

This paper presents results of tests performed to characterize the physical and chemical properties of five blast-furnace slags having MnO content up to 21%. The interactions between ordinary Portland cement or calcium oxide and each slag were investigated by X-ray diffraction, scanning electron microscopy, and thermoanalysis. Mortars and concretes using these slags were cast. When ground to a Blaine surface area of 300 m^2/kg, the slags were utilized in road binders in combination with calcium oxide or Portland cement. When ground to a Blaine surface area of 600 m^2/kg, the slags were introduced into the composition of different concretes instead of fly ash or silica fume. Based on the resulting high strengths, fine grinding of manganese-rich slag for use in concrete appears to be a good way of beneficiation.

Keywords: Blast-furnace slag; Compressive strength; Concrete; Grinding; Manganese; Microstructure

Excellent reviews of the physicochemical and mineralogical characteristics of slag and slag cement have been reported [1–4]. The influence of chemical composition, mineralogy, glass content, and other activity parameters on the hydraulic properties of slag have been recognized. For example, the influence of Al_2O_3 (up to 13%) and MgO (up to 11%) were reported to increase the strength, but the role of MnO has not yet been clearly established.

Because manganese (Mn) can occupy sixfold coordination, it stabilizes the glassy phase of slag but reduces its hydraulic activity [5,6]. The prediction of mechanical strength at different ages has been attempted by many workers using chemical indexes, also called hydraulic moduli. Many attempts have been made to assess slags on the basis of the following modulus: $(CaO + MgO + Al_2O_3)/SiO_2$. This and similar moduli express that hydraulic activity is broadly favored by more basic composition, but the effect of Al_2O_3 content is complex and none of the proposed moduli have proved valid for the detailed comparison of slags other than those of relatively similar compositions produced within a given plant. Some new moduli presented at the 7th International Congress on the Chemistry of Cement in Paris (1980) by Smolczyk [1] take into account the entire chemical analysis, including minor elements. Two of them, referred to F_8 [7] and F_9 [8] by Smolczyk, consider a negative influence of MnO as given in Eqs. (1) and (2):

$$F_8 = \frac{C + 0.5M + A + CaS}{S + MnO} \quad (1)$$

$$F_9 = \frac{C + 0.5M + A}{S + FeO + (MnO)^2} \quad (2)$$

where C = CaO, M = MgO, A = Al_2O_3, S = SiO_2, and CaS = oldhamite.

Taneja et al. [9] showed that blended cements produced by grinding together granulated slag containing MnO as high as 6.75%, clinker, and gypsum complied with the requirements of Indian standard specifications; hence, such slags were suitable for manufacture of cement. However, 3- and 7-day strengths of slag cements were much lower than those of control Portland cement. Lowering of strength was not correlated with MnO or CaO or CaO + MgO. It appeared that, apart from chemical composition, the conditions of granulation, namely, temperature and speed, play an important role in deciphering the quality of slag.

Gakhariya et al. [10] reported higher rates of hydration and strength development for concrete with the addition of ferromanganese, a waste product from the ferroalloy industry. The material also improved the workability of concrete.

A study was undertaken to assess the properties of five ground granulated blast-furnace slags produced by the ferroalloy industry. These slags are characterized by a high Mn content (MnO ranges from 5.4–21%) and their granulation

* Corresponding author. Tel.: 33-4-7243-8296; Fax: 33-4-78949807.

0008-8846/99/$–see front matter
PII: S0008-8846(98)00096-9

Table 1
Chemical composition of slags

Oxides (%)	Mn-rich slags S_1	S_2	S_3	S_4	S_5	Typical slag
SiO_2	17.4	21.3	20.2	20.4	37.1	34.3
Al_2O_3	27.0	21.4	23.8	23.0	22.6	12.4
$F3_2O_3$	0.3	0.1	0.3	0.4	1.2	0.9
MnO	5.4	12.5	15.9	21.0	12.3	0.1
MgO	7.2	8.1	7.1	6.9	8.6	8.3
CaO	34.7	35.0	30.7	29.0	17.1	43.7
Na_2O	1.6	0.4	0.5	0.2	0.4	0.3
K_2O	—	0.1	0.1	0.1	1.5	0.3
TiO_2	0.2	0.3	0.4	0.5	0.1	0.6
P_2O_5	0.2	0.2	0.1	0.2	0.3	0.2
SO_3	5.0	3.4	2.9	2.6	2.4	3.0
Cl	2.8	0.5	0.7	0.2	0.1	—
LOI	2.9	−1.8	−1.5	−3.0	−2.8	−1.5

is achieved using seawater, which results in a high Cl^- concentration in some samples.

The study was divided in three parts:

1. Slags were ground to a Blaine specific surface area of 300 m^2/kg and their activation by either quicklime (CaO) or ordinary Portland cement (OPC) was investigated. The goal of this research was to verify if Mn-rich slag should be suitable for the development of binders for road sub-base stabilization.
2. Slags were ground to a Blaine surface area of 400 m^2/kg to improve their activity and activated by cement. The compressive strength of mortars and the microstructure of pastes were investigated as the cement-to-slag (C/S) ratio varied from 0.08 to 0.50. This study allows assessment of the influence of MnO content on the reactivity of the slag.
3. Finally, a more acid (silica-rich) slag was ground to a Blaine surface area of 600 m^2/kg and used as ultrafine admixture in different concretes, leading to very good results.

1. Experimental

1.1. Materials

1.1.1. Slags

The chemical composition of each sample is listed in Table 1. Samples S_1 to S_4 were supplied by the same plant. Table 1 also lists the chemical composition of a typical slag used in the cement industry. From Table 1, it appears that:

- Mn-rich slags present lower SiO_2 and CaO contents and greater Al_2O_3 contents than the typical slag,
- The MnO content ranged from 5.4% to 21.0% in samples S_1 to S_5,
- In these samples, the chloride content was in the range of 0.1% to 2.8%.

As shown by X-ray diffraction (XRD) (Fig. 1), samples S_1 to S_5 are essentially composed of a glassy phase. In sample S_1, halite (NaCl) is present as crystallized phase, whereas potassium sulfide (K_2S) is detected in sample S_5.

For slags S_1 to S_4, XRD patterns show an asymmetric diffuse band from the glass peaking at about $2\vartheta = 32°$ and extending from about 23° to 36°. For S_5, the position of the diffuse scattering maximum (glass "hump") is shifted to a smaller 2ϑ value ($2\vartheta = 29°$) due to the higher silica content of S_5.

The chemical moduli of the different slags are listed in Table 2.

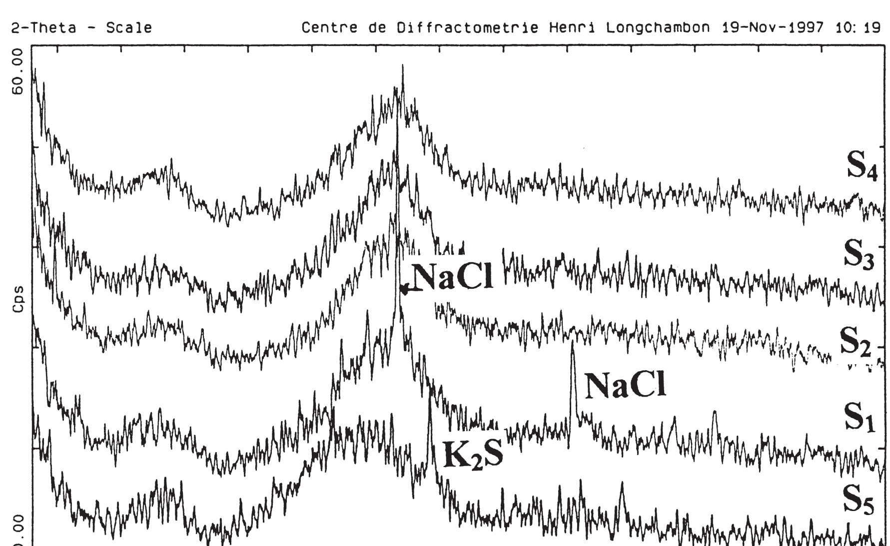

Fig. 1. X-ray diffraction spectra of Mn-rich slags.

Table 2
Chemical moduli of slags

Modulus	Mn-rich slags					Typical slag
	S_1	S_2	S_3	S_4	S_5	
$F_1 = C/S$	1.99	1.64	1.52	1.42	0.46	1.27
$F_2 = (C + M)/S$	2.41	2.03	1.87	1.76	0.69	1.52
$F_3 = (C + M)/(S + A)$	0.94	1.01	0.86	0.82	0.43	1.11
$F_8 = (C + 0.5M + A)/(S + MnO)$	2.86	1.79	1.61	1.34	0.89	1.75
$F_9 = (C + 0.5M + A)/(S + (MnO)^2)$	1.40	0.34	0.21	0.12	0.23	1.76

Table 3
Physical properties of slags used in the first series of tests

Slag	Blaine specific surface area (m^2/kg)	Average diameter of the particle size distribution D_{50} (μm)
S_2	315	15.0
S_4	280	10.0
S_5	298	9.5

Usual slag and samples S_1 to S_4 are basic (C/S >1), whereas S_5 is acid (C/S <1). According to Keil [7], slags of index $F_8 > 1.5$ (samples S_1 to S_3) have good hydraulic properties, whereas those <1.5 (samples S_4 and S_5) have moderate hydraulicity.

1.1.2. Activators

Quicklime (CaO) supplied by PROLABO and ordinary Portland cement (CEM I 52.5) were used as activators.

1.2. Experimental program

1.2.1. Development of a binder for road sub-base stabilization

In such a binder, the amount of activator is kept very low to reduce its cost. Slags S_2, S_4, and S_5 were ground to a Blaine surface area of about 300 $m^{2/}$/kg and activated by either 4% CaO or 8% OPC. S_1 and S_3 were not considered for this application because of their limited availability. The physical properties of the investigated slags are listed in Table 3.

Table 4
Physical properties of slags used in the second series of tests

Slag	Specific gravity	Blaine specific surface area (m^2/kg)	Average diameter of the particle size distribution (μm)
S_1	2.88	405	33.0
S_2	3.00	400	13.0
S_3	3.09	384	14.5
S_4	3.17	380	9.0

Table 5
Mixture proportions of the mortars of the second series of tests

Mortar	Binder (B)		Sand (g)	Water (g)	W/B
	Slag (g)	Cement (g)			
M1	450	36	1350	225	0.463
M2	422	64	1350	225	0.463
M3	389	97	1350	225	0.463
M4	324	162	1350	225	0.463

Mortars containing the activated slag were cast with a sand-to-binder ratio of 3 and a water-to-binder ratio of 0.50. The binder was composed of slag and calcium oxide. The compressive strength of these mortars was measured after 7, 28, and 90 days of hydration. For curing, the mortars were demolded after 3 days of hydration and immersed in lime-saturated water until the day of mechanical testing.

Pastes of activated slag were prepared at standard consistency and their hydration mineralogy and microstructure investigated by differential thermal analysis (DTA), XRD, scanning electron microscopy associated with energy dispersive X-ray analysis, and mercury intrusion porosity.

1.2.2. Influence of MnO content on slag reactivity

Slags S_1 to S_4 were ground to get a Blaine surface area of about 400 m^2/kg and activated by different amounts of OPC. C/S ratio ranged from 0.08 to 0.50. Due to its ex-

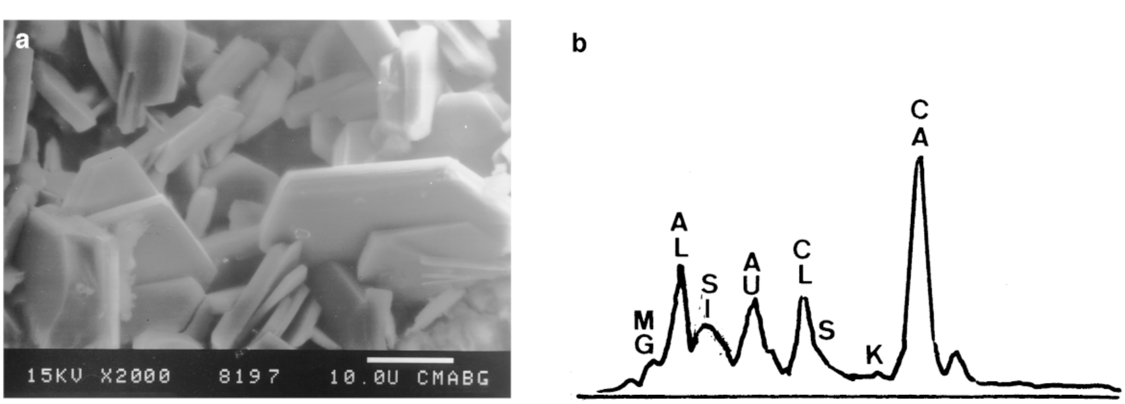

Fig. 2. (*a*, *b*) Chloroaluminate in S_2 activated by cement.

Table 6
Performances of mortars containing Mn-rich slag activated by CaO (4%) or OPC (8%)

Activator	Slag	Compressive strength (MPa) 7 days	28 days	90 days
Quicklime	S_2	4.7 ± 0.1	9.3 ± 0.1	12.0 ± 0.4
	S_4	3.8 ± 0.2	10.5 ± 0.2	29.8 ± 0.4
	S_5	0.2	1.5 ± 0.4	11.9 ± 0.9
Cement	S_2	9.9 ± 0.1	14.1 ± 0.4	17.5 ± 0.8
	S_4	0.6	23.5 ± 0.8	31.6 ± 1.7
	S_5	2.9 ± 0.5	7.0 ± 0.2	15.1 ± 0.4

Table 7
Compressive strength of mortars cast with slags ground to a Blaine surface of 400 m^2/kg

Slag	MnO (%)	Compressive strength (MPa) 3 days	7 days	28 days
S_1	5.4	8.1 ± 0.1	11.5 ± 0.3	14.4 ± 0.4
S_2	12.5	3.6 ± 0.1	12.2 ± 0.2	17.6 ± 1.2
S_3	15.9	3.0 ± 0.1	11.4 ± 0.1	16.2 ± 0.4
S_4	21.0	0.5	2.3 ± 0.1	25.1 ± 0.8

Cement/slag = 0.08.

pected low hydraulic activity (C/S = 0.46 < 1), slag S_5 was not considered in this study. The physical properties of the slags are presented in Table 4.

The mixture proportions of mortars are given in Table 5. The hydration mineralogy and microstructure of these mortars also were investigated.

1.2.3. Utilization of slag S_5 as an ultrafine component of concrete

Slag S_5 was ground to a Blaine fineness of 600 m^2/kg and used in different types of concretes, in comparison with fly ash or silica fume.

2. Results and discussion

2.1. Utilization of Mn-rich slag for road sub-base stabilization

The results of compressive strength measurements are listed Table 6. The best long-term strengths are obtained with slag S_4, which has the highest MnO content. For this slag, the early-age strengths are very low. Lower levels of strength are obtained with S_2 and S_5, except at early age when activated by cement. The MnO content in S_2 and S_5 samples is about the same; these slags essentially differ from one another in the C/S ratio: S_2 is basic whereas S_5 is acid. From these results, two conclusions may be drawn:

1. The chemical modulus C/S ratio alone is not sufficient to predict the hydraulic activity of Mn-rich slags, and
2. Manganese seems to have a negative influence on the reactivity and strength of slag at early age, but it does not hinder long-term activation.

The characterization of the pastes can be summarized as follows:

- The microstructure generally was badly crystallized; its composition was isomorphous of that of the slag;
- XRD and DTA did not reveal any residual calcium hydroxide after 28 days of hydration;
- XRD (peaks at $2\vartheta = 11°$ and $31°$) and DTA (endothermic peaks at 200 and 350°C) detected the precipitation of chloroaluminate, as S_2 was activated by either 4% CaO or 8% OPC. The morphology of this hydrate and its composition are shown in Fig. 2.

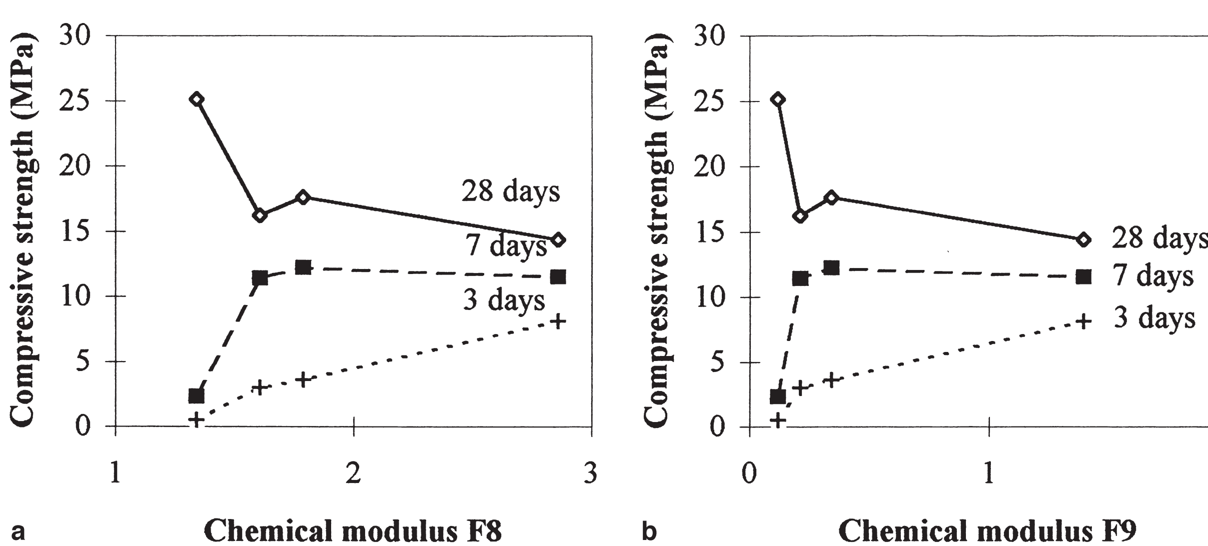

Fig. 3. (*a*, *b*) Evolution of the compressive strength of mortars vs. chemical moduli.

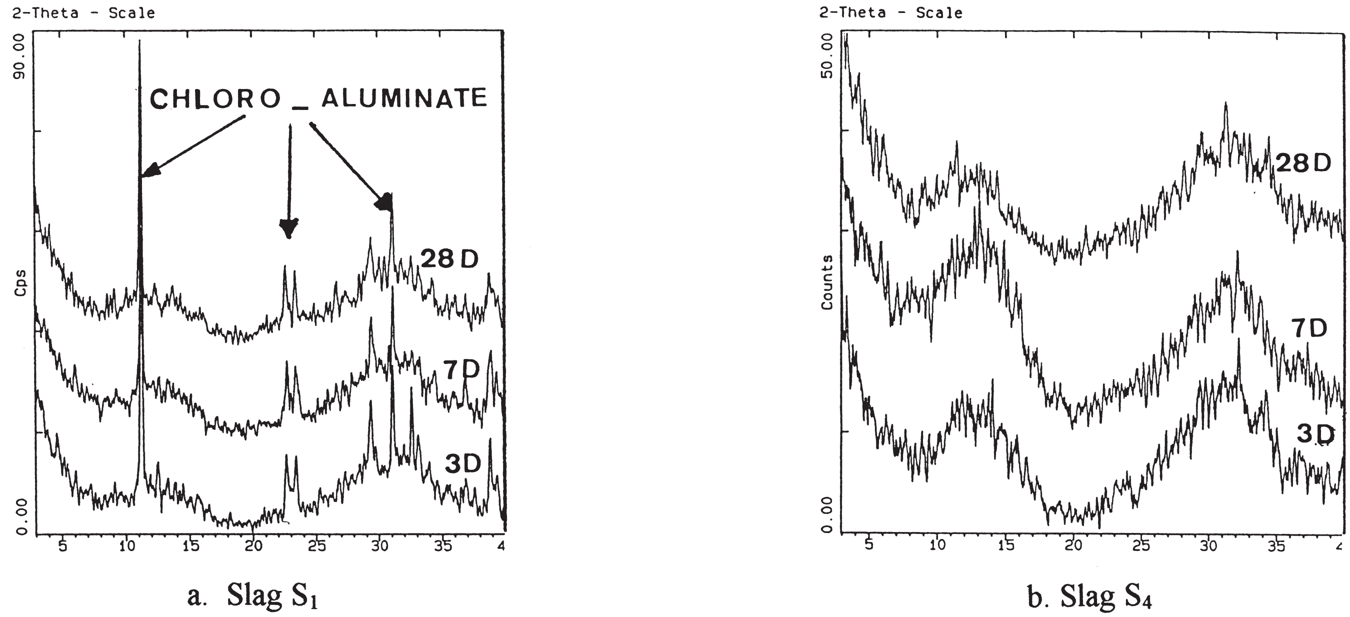

Fig. 4. X-ray diffraction patterns of mortars containing slags S_1 (*a*) and S_4 (*b*) activated by 8% cement.

2.2. Influence of MnO content on slag reactivity

The mechanical performance of mortars cast with slags S_1 to S_4 ground to a Blaine fineness of about 400 m^2/kg (Table 4) and activated by 8% cement is shown in Table 7. Table 7 shows that, except for slag S_2, the higher the MnO content, the lower the early-age strength and the higher the long-term strength. These results confirm those presented in Table 6. High levels of manganese seem to inhibit the early-age activity of the slag.

As shown in Fig. 3, there is no relationship between compressive strength and chemical moduli F_8 and F_9. As reported by Taneja et al. [9], such indexes are recommendations only and hydraulicity depends on the conditions of granulation of slags.

XRD investigations (Fig. 4) showed that:

- No hydrate was detected at 3 days in the mortar cast with S_4,
- Chloroaluminate precipitated in mortars containing slags S_1 to S_3, whatever the time of hydration might be, and
- All portlandite was consumed after 28 days of hydration.

To study the influence of cement content on the compressive strength of mortars, slags S_1 (minimum MnO content) and S_4 (maximum MnO content) were activated by various amounts of cement; the C/S ratio ranged from 0.08 to 0.50. The results are presented in Table 8.

Mortars containing slag S_1 exhibit better strengths up to 7 days of hydration than mortars containing slag S_4. The increase in Blaine fineness has no influence on the hydraulicity of slag S_4. Whatever the cement content is, the strengths remain low for mortars containing slag S_4 within the first 7

Table 8
Influence of the cement content on the compressive strength of mortars

Slag	Cement/slag	Compressive strength (MPa) 3 days	7 days	28 days
S_1	0.08	8.1 ± 0.1	11.5 ± 0.3	14.4 ± 0.4
	0.15	9.8 ± 0.2	11.6 ± 0.3	14.7 ± 0.4
	0.25	12.3 ± 0.2	14.3 ± 0.3	18.3 ± 0.2
	0.50	17.7 ± 0.5	20.5 ± 0.6	23.9 ± 0.4
S_4	0.08	0.5 ± 0.1	2.3 ± 0.1	25.1 ± 0.8
	0.15	0.4 ± 0.1	3.0 ± 0.1	28.7 ± 0.1
	0.25	0.4 ± 0.1	3.4 ± 0.1	30.3 ± 0.4
	0.50	1.5 ± 0.1	16.4 ± 0.3	38.0 ± 1.7

Table 9
Increase in strength of mortars (MPa) between 3 and 28 days

Slag	Cement/slag 0.08	0.15	0.25	0.50
S_1	+6.3	+4.9	+6.0	+6.2
S_2	+24.6	+28.3	+29.8	+36.5

Table 10
Comparison between quartz and slag

Material	Compressive strength (MPa) 3 days	7 days	Increase in strength (MPa)
S_1	17.7 ± 0.5	20.5 ± 0.6	+2.8
S_4	1.5 ± 0.1	16.4 ± 0.3	+14.9
Quartz	7.8 ± 0.3	10.0 ± 0.1	+2.2

Cement/slag or quartz = 0.50.

Table 11
Performance of concretes containing S_5 slag ground to 600 m^2/kg

	C_1	C_2	C_3	C_4	C_5	C_6
Mixture proportions (kg/m^3)						
Cement	190	190	350	300	450	450
Slag S_5	—	70	—	50	—	50
Fly ash	110	—	—	—	—	—
Silica fume	—	—	—	—	31.5	—
Sand 0/4 mm	880	880	785	785	800	800
Gravel 4/20 mm	920	920	1,070	1,070	1,100	1,100
Plasticizer	1.08	1.08	—	—	—	—
Superplasticizer	—	—	—	—	13.5	13.5
Water	205	195	200	200	170	165
Slump (mm)	160	180	180	140	200	>200
Compressive strength (MPa)						
1 day	2.8	4.5	15.2	13.9	25.5	28.1
7 days	16.5	21.1	32.4	36.3	61.8	67.6
28 days	24.7	32.8	42.0	49.3	81.7	85.3
90 days	30.5	37.5	44.0	50.4	83.5	88.3

days of hydration. Slag S_4 seems to inhibit cement hydration at early age. After 28 days of hydration, good strengths are obtained with slag S_4 when the cement content is higher than 25%.

As shown in Table 9, the increase in strength between 3 and 28 days of hydration is different for slags S_1 and S_4.

For mortar cast with S_1, the average increase in strength is about 6 MPa, whatever the C/S ratio is. When S_4 is used, the increase in strength depends on the C/S ratio and is maximum when slag is activated by 50% cement. To understand this phenomenon, slag was replaced by fine quartz in the composition containing 50% cement, and compressive strengths were measured after 3 and 7 days. The results are presented in Table 10. From Table 10, it appears that the modest increase in strength is the same for quartz and slag S_1, and this increase can be attributed to increasing cement hydration between 3 and 7 days. For S_4, this increase is much greater, and the increase can be linked to chemical reactions involving the slag starting at 7 days.

2.3. Utilization of slag S_5 as ultrafine additional material in concrete

Slag S_5 was ground to a Blaine fineness of 600 m^2/kg and introduced into three types of concretes:

1. As fly ash replacement in conventional concrete intended for building construction with an average 28-day compressive strength of 25 MPa,
2. As cement replacement in concrete for civil projects (35 MPa), and
3. As silica fume replacement in high-strength concrete (>60 MPa).

Table 12
Water permeability of concretes C_1 to C_6

	C_1	C_2	C_3	C_4	C_5	C_6
Water permeability (10^{-12} m/s)	74	63	3.5	3.9	0.97	0.25

The mixture proportions, workability, and strengths of these concretes are listed in Table 11.

No carbonation was observed in concretes C_2 to C_6, and the water permeabilities of concretes (an average from three measurements) C_1 to C_6 are listed in Table 12.

The use of slag S_5 ground to a Blaine fineness of 600 m^2/kg leads to very good strength and low permeability.

3. Conclusions

From the limited investigation carried out in the present study, the following conclusions can be drawn:

1. Mn-rich slags can be used in binders for road subbase stabilization when they ground to a Blaine fineness close to that of cement (300 m^2/kg).
2. High levels of MnO seem to inhibit the early-age hydration of cement but have no negative influence on long-term properties.
3. An increase in fineness of slags containing >20% MnO has no influence on their hydraulicity at early age.
4. A good beneficiation of Mn-rich slag is to grind it to a Blaine specific area of 600 m^2/kg and introduce it as additional ultrafine material in concrete.

References

[1] H.G. Smolczyk, Slag structure and identification of slag, Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, Volume I, 1980, pp. III.1/3–1/17.

[2] M. Daimon, Mechanism and kinetics of slag cement hydration, Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, Volume I, 1980, pp. III.2/1–2/9.

[3] M. Regourd, Caractéristiques et activation des produits d'addition, Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Volume I, pp. 190–229, (1986).
[4] H. Uchikawa, Effect of blending components on hydration and structure formation, Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Volume I, 1986, pp. 249–280.
[5] K. Chopra, C.A. Taneja, Co-ordination state of aluminium, magnesium and manganese ions in synthetic slag glasses, VISCC, Tokyo, Volume IV, 1968, pp. 228–236.
[6] S.M. Royak, V.F. Krylov, V.S. Klimenteva, Investigations on hydraulic reactivity of slags with high contents of manganese and barium, Stroitelniye Materialy 3 (1965) 37–39 (in Russian).
[7] F. Keil, Slag cements, Proceedings of the 3rd International Congress on the Chemistry of Cement, London, 1952, pp. 549–550.
[8] H. Sopora, Bewertung von Rochofenschlacken für die Zementherstellung im betriebslaboratorium, Silikattechnik 10 (1959) 361–363.
[9] C.A. Taneja, S.P. Tehri, M. Singh, High manganese, high alumina slag for cement manufacture, Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, Volume II, 1980, pp. III-48–III-51.
[10] R.V. Gakhariya, A.I. Daneliya, B.N. Malyshev, Partial replacement of cement by ferroalloy manufacturing wastes in hydraulic-engineering concretes. Energ Stroit 6 (1989), 12–13; Chemical Abstracts 111 (1989) 179760 h.