

# Effects of Moisture on Surface Chemistry of Steel Slags and Steel Slag-Asphalt Paving Mixes

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Random cracking and premature failure have been observed in some steel slag-asphalt pavements in Ontario. The causes of the failure were investigated. Surface chemistry and morphology of steel slags and asphalt mixes and the effect of moisture on these characteristics were studied using scanning electron microscopy, scanning electron microscopy coupled with energy-dispersive x-ray analysis, and optical microscopy. X-ray diffraction and electron microprobe analysis were used for mineralogical studies. Experiments were also performed to determine moisture uptake and volume expansivity of steel slags and steel slag-asphalt mixes. Basic oxygen furnace slags and an electric arc furnace slag were used in this investigation, and asphalt mixes were prepared from some samples. The results indicate that failure in steel slag-asphalt mixes in moist environments is due to the formation of calcium-rich deposits, mainly calcium carbonate, along the surface and the interface. This affects interfacial bonding and can cause excessive expansion of the slag leading to cracking of the mixture. This reactivity was also observed in field core samples, even after several years of service. The mineralogical data showed that the distribution and microstructure of the two main phases (an iron oxide-rich mixed oxide phase and a calcium silicate phase in steel slags) were different among the slags examined. The calcium silicate phase appears to be one of the sources responsible for the reactivity of steel slags in moist environments.

Steel slag aggregates (SSA) were first used in hot-mix asphalt (HMA) pavement in Ontario in 1969. They were used primarily as premium skid-resistant aggregates in dense friction course (DFC), open friction course (OFC), and other densely graded hot-laid asphalt pavements (1). Although steel slag is not used as extensively as other aggregates, there have been a number of successful applications in different highway environments. Observations of premature road surface failures, mainly in the form of random cracking, have raised concerns about the overall strategy of using steel slag-asphalt mixtures and have limited their application.

Many studies concerning use of steel slag in asphalt mixes pertained to the application of these materials and their effect on the properties and performance of the asphalt (2,3). Typical mix properties discussed include skid resistance, cracking behavior, and tensile characteristics. The main concern about steel slag properties is their volume expansion characteristics, primarily attributed to the amount of "free" lime (CaO) and/or magnesium oxide (MgO) present in the slag (2,4). In many reviews of the use of steel slag as an aggregate, its composition is given in a summary table that only outlines the expected bulk chemical composition, but the role of

changes in steel slag composition and surface properties, particularly the effects of moisture on surface properties has not been addressed adequately.

Many studies of steel slag properties and composition variations originated in the steel industry (5). These reports provide details about specific steel-making practices and their effect on slag chemistry, but, again, surface reactivity has not been considered. A master's thesis published at McMaster University in 1981 (6) considered weathering reactions on aggregate surfaces and their effects on skid resistance, but unfortunately there is no detailed follow-up to this work. There appears to have been little other work on the surface chemistry of steel slags (7).

Some research was performed to evaluate the degree of asphalt oxidation in relation to aggregate interaction (8) and the effect of moisture on asphalt-aggregate mixes (9,10), but these studies have focused on analytical technique development or evaluation of testing methods and are not related directly to the interaction of aggregate chemistry and asphalt-aggregate interfaces.

The way in which surface chemistry changes upon exposure to environmental variables may have some effect on the interfacial adhesion properties of the steel slag. Also, the relationship between the mineralogy of steel slags and their surface reactivity has not been investigated.

The main objective of this study was to gain fundamental knowledge about the processes occurring at the steel slag surface and near-surface regions during exposure of steel slag and steel slag-asphalt mixes to various environmental variables, particularly moisture.

## METHODOLOGY

### Steel Slag Samples Studied

The steel slag samples examined in this study were produced by two different steel-making techniques. Samples A through E were produced in a basic oxygen furnace (BOF), whereas sample F was produced in an electric arc furnace (EAF). Three of the BOF slags (B, D, E) were typical slags from three different plants; the other two BOF slags (A, C) were experimental samples.

DFC Marshall briquettes were made from three types of BOF slags representing typical slag from two sources (B, D) and an experimental slag (A), along with a traprock reference sample, using Marshall mix design procedures. Attempts to make DFC briquettes from EAF slags were not successful because of difficulty in compacting to 3 percent air voids.

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## Instrumentation

Three techniques were primarily used in this study: (a) scanning electron microscopy coupled with energy dispersive x-ray analysis (SEM/EDX), (b) electron probe x-ray microanalysis (EPMA), and (c) x-ray diffraction (XRD). These techniques provide complementary information about material composition, morphology, and surface chemistry.

A modern SEM (Model ISI D-130) with a Noran light element EDX system capable of quantitative analysis and digital x-ray mapping available at Surface Science Western was used. The EPMA instrument used was a JEOL Superprobe 8600. A Rigaku Rotaflex Ru-200B spectrometer from the Department of Earth Sciences, University of Western Ontario (scan conditions: 2 degrees to 100 degrees (2 $\theta$ ) with a step size of 0.020 degrees) was used for XRD measurements.

Some Fourier transform infrared (FT-IR) measurements were also performed. These measurements were performed with a Perkin Elmer 2000 FT-IR apparatus and, in some cases, a Spectra-Tech baseline horizontal attenuated total reflectance (ATR) accessory was used. In the ATR the solid sample was pressed against a ZnSe crystal.

## Sample Preparation

For all SEM analysis, the steel slag samples were mounted on sample holders using carbon paint and then coated with a thin layer of sputter-deposited gold to minimize charging effects.

For the microprobe analysis, samples of each steel slag under study were mounted in a cold mount epoxy resin (Struers Epo-Fix) and polished using standard metallographic methods to a 3- $\mu$ m diamond finish. After polishing, the cross sections were coated with a thin layer of evaporated carbon and then examined using the electron microprobe.

For the XRD analysis, the slag samples were crushed (jaw crusher), placed in a ball mill, and ground by mortar and pestle to  $\sim 10\text{-}\mu\text{m}$  particle size. The samples were then mounted on a glass slide and placed in the diffractometer.

Bulk chemical composition of steel slag samples was determined by wet chemical analysis using a partial digestion procedure with finely ground samples. Free lime content was estimated by an ethylene glycol-methanol extraction and titration procedure. Physical properties relevant to use of steel slag as aggregate were also determined.

## Moisture Uptake and Expansion Tests

Tests for percentage mass increase of steel slag caused by moisture uptake under different relative humidities were conducted in the laboratory using saturated salt solutions in desiccators maintained at ambient temperature.

A steel slag expansion test was performed according to ASTM D-4792-88. In this procedure steel slag specimens were prepared using the standard Proctor method and stainless steel molds with perforated base plates to allow for moisture movement during the immersion period. The specimens were then immersed in the water bath and maintained at  $71^\circ\text{C} \pm 2^\circ\text{C}$ , and the vertical expansion with time was recorded daily for 2 weeks.

Steel slag-asphalt briquettes with 8 to 10 percent air voids were also prepared to conduct HMA expansion tests (11).

## Weathering Experiments

Two accelerated weathering experiments were performed: the first set involved only slag particles exposed to 90 to 100 percent RH at  $30^\circ\text{C}$ ; the second set involved both asphalt Marshall briquettes and slag particles exposed to 100 percent RH at  $50^\circ\text{C}$ . In each experiment, each slag sample or briquette was placed in an open beaker, and the beaker was placed in the humidity chamber. In the humidity chamber the samples were observed to be continuously wet with a thin film of water but were never completely immersed.

## RESULTS

### Steel Slag Surface Characterization

Results of surface characterization by EDX are summarized in Table 1. The results show surprising consistency in the surface composition of the different steel slags. The sampling depth for EDX analysis is 1 to 2  $\mu\text{m}$  under these conditions, so the term "surface" actually refers to the average composition to this depth below the surface. In all cases, surfaces were enriched in calcium and oxygen with varying levels of silicon, iron, aluminum, magnesium, and manganese. In most cases, surface carbon levels were below 10 wt percent. On average, surface calcium levels decreased and oxygen levels increased after washing.

Figure 1 shows a series of SEM micrographs of the surface of as-received steel Slag D (a,b) and the same slag after washing (c,d). Washing appears to have removed larger crystals from the surface, giving a more uniform topography. These changes in surface chemistry and surface morphology after washing indicate that washing effectively removed loosely attached material resulting in lower surface calcium levels. However, there is evidence of additional surface reactions, as shown by development of a network of finer crystals on the washed slag surfaces (Figure 1d). As with the EDX results, these changes in surface morphology were found to be consistent among the slags investigated.

### Cross-Section Characterization by EPMA

Results of microprobe analysis on the slag samples are summarized in Table 2, a and c. Also, representative backscattered electron images were collected of both the bulk (i.e., slag particle interior) and the interface region; these are shown in Figure 2.

As shown in Figure 2(a) and (b), the slag was not uniform in cross section. In this case, the cross section is from steel Slag D, but with the exception of the EAF slag sample [Figure 2(c) and (d)], the observations were consistent among all slag samples examined. The backscattered images indicate at least three distinct phases in the slag: a light-colored phase [1 in Figure 2(a)], a dark-colored phase (2), and a medium-colored phase (3). All the slags appear to have phases 1 and 2, but only slag D exhibited phase 3. In addition to the various phases present in the bulk of the slag particles, it is clear from Figure 2(b) that the interface region of the slag is different again.

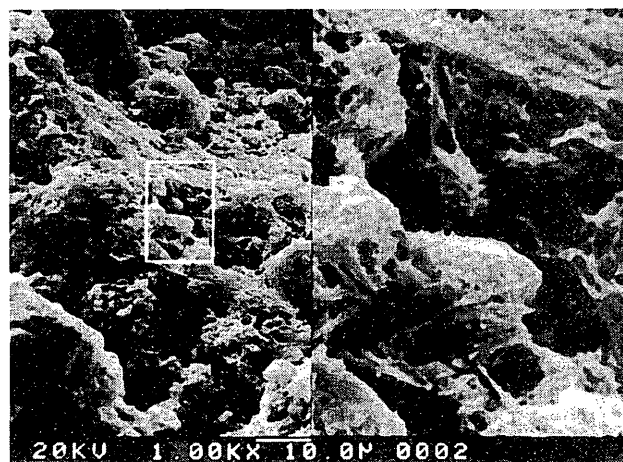
The results shown in Table 2(a) for slag D demonstrate that the light-colored phase is an iron oxide-rich phase of mixed oxides of magnesium, manganese, and calcium. In contrast, the dark phase was a calcium oxide-rich phase also high in silicon oxide, probably a form of calcium silicate. The medium phase (3) was consistent

**TABLE 1** Composition of Steel Slag Surfaces by EDX Analysis

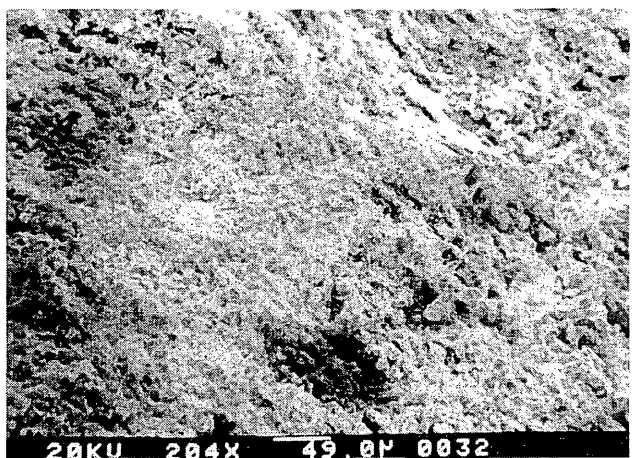
Sample	Treatment	Element (wt%)							
		Ca	Fe	Al	Si	Mg	Mn	C	O
A	MTO Washed	44.0	16.0	0.9	5.4	2.2	3.3	1.8	27.0
B	MTO Washed	32.0	4.4	1.7	6.3	2.2	1.2	5.9	47.0
C	MTO Washed	40.0	3.5	0.4	1.5	1.3	2.2	11.0	40.0
D	MTO Washed	35.0	4.9	0.6	5.0	2.5	2.0	8.2	42.0
	As Received	42.0	3.1	0.3	5.7	1.7	2.4	8.0	37.0
F	As Received	46.0	2.7	2.7	10.0	2.9	1.4	0.0	35.0



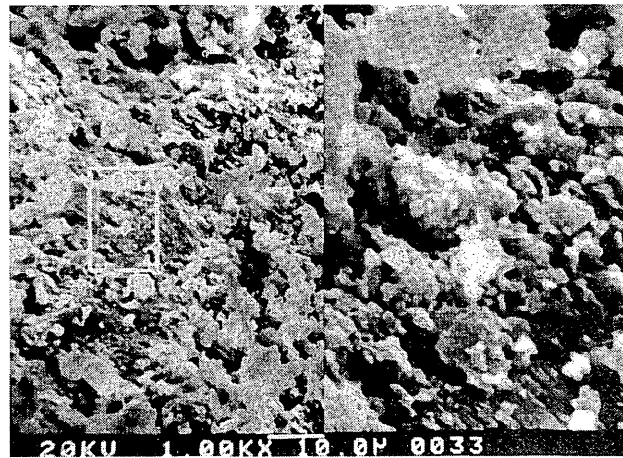
(a)



(b)



(c)



(d)

**FIGURE 1** SEM micrographs of Slag D: (a) as received under low magnification; (b) as received under high magnification; (c) washed, under low magnification; (d) washed, under high magnification.

TABLE 2 Analysis of Steel Slag Cross Sections by Electron Microprobe

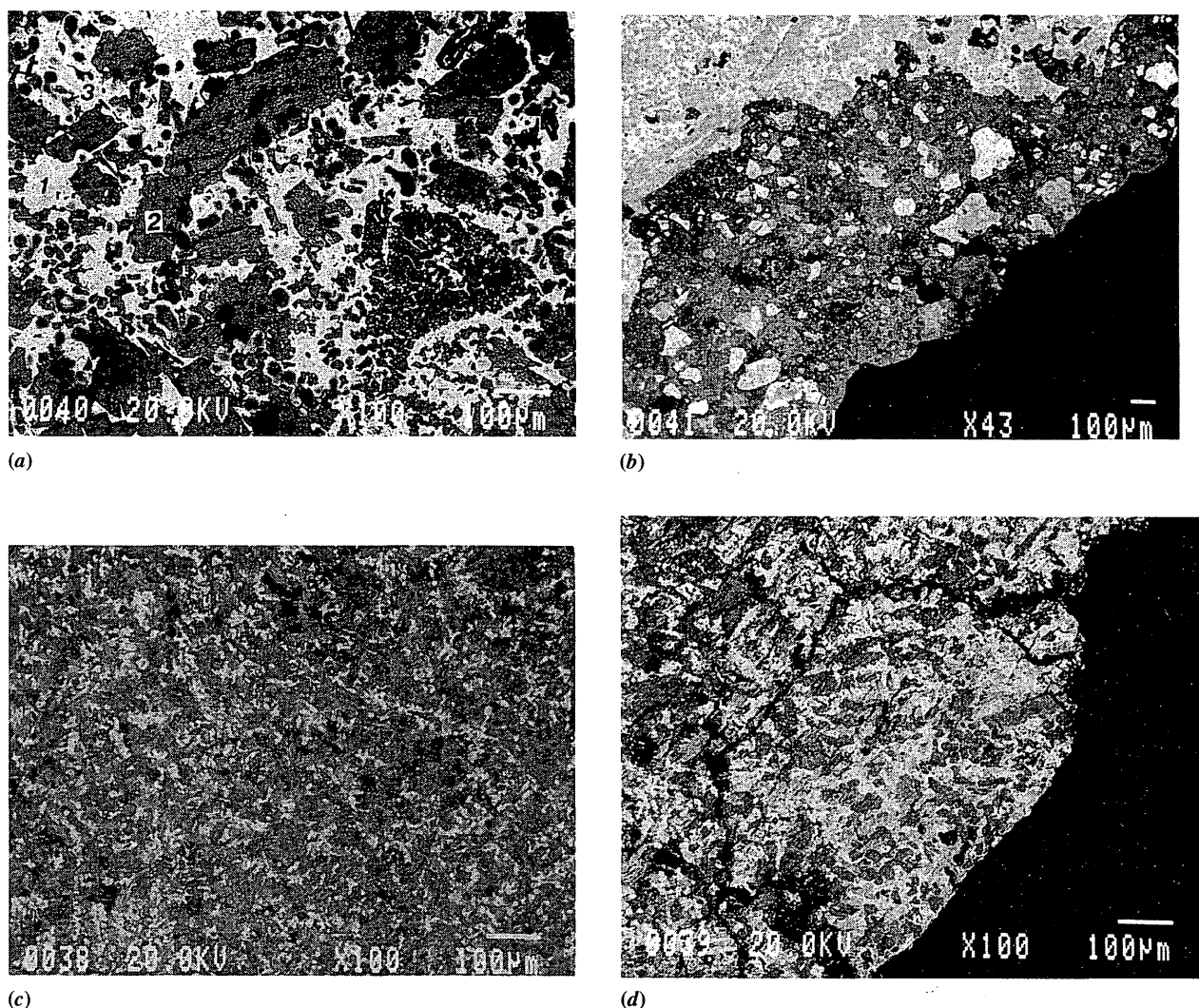
(a) Slag D	Constituent (wt%)						
Region/Phase	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	MnO	Other
Light #1	—	—	66.0	7.3	14.0	11.0	
Light #2	0.8	—	58.0	19.0	8.6	13.0	
Light #3	—	—	48.0	32.0	5.2	15.0	
Medium #1	2.2	2.8	45.0	0.6	45.0	1.1	TiO <sub>2</sub> 3.0
Dark #1	32	0.3	4.6	0.7	61.0	1.6	
Dark #2	25	0.2	5.5	0.9	66.0	1.7	
Dark #3	27	0.2	4.2	1.0	67.0	1.4	
Edge #1	12.0	—	8.6	3.6	65.0	10.0	
Edge #2	32.0	0.2	4.2	0.8	60.0	2.3	
Edge #3	36.0	0.8	11.0	1.3	44.0	6.0	Cl 0.9
Edge #4	22.0	23.0	4.4	4.7	43.0	1.4	Cl 0.7
Edge #5	0.5	—	26.0	53.0	2.0	18.0	

(b) Slag E	Constituent (wt%)						
Region/Phase	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	MnO	Other
Light #1	1.1	3.5	44.0	0.8	44.0	3.1	TiO <sub>2</sub> 3.1
Light #2	3.2	8.1	36.0	0.8	46.0	2.3	TiO <sub>2</sub> 3.8
Dark #1	32.0	0.3	2.1	0.3	63.0	0.5	TiO <sub>2</sub> 0.3
Dark #2	33.0	0.4	1.8	0.3	64.0	0.5	
Dark #3	34.0	0.2	1.2	0.5	63.0	0.5	
Edge #1	3.4	0.4	0.5	0.8	94.0	0.4	Cl 0.3
Edge #2	24.0	4.1	4.1	13.4	52.0	0.8	Cl 1.7
Edge #3	15.0	1.8	9.1	8.0	62.0	2.7	Cl 1.7
Edge #4	15.0	15.0	2.2	3.9	63.0	0.2	Cl 0.2

(c) Slag F	Constituent (wt%)						
Region/Phase	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	MnO	Other
Light #1	—	—	28.0	37.0	7.0	28.0	
Light #2	—	—	24.0	40.0	8.1	28.0	
Light #3	—	—	29.0	41.0	4.1	26.0	
Dark #1	38.0	0.6	0.2	3.2	58.0	—	
Dark #2	33.0	0.4	0.3	4.1	62.0	—	
Dark #3	30.0	0.4	0.2	4.5	65.0	—	

with a calcium oxide, possibly a calcium ferrite phase such as Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> or CaFeO<sub>2</sub>, which is also a constituent in the light-colored mixed oxide phase. The detailed composition, distribution, and microstructure of the primary phase was found to be different among the slags, probably a function of the type of processing to which the slag was subjected (cooling rate probably being the dom-

inant processing difference). In some regions of the slag bulk interiors, particularly in and near internal pores, there were regions of 90 to 100 percent calcium oxide, perhaps representing a small amount of free lime in the slag. However, these regions were normally less than 1 to 2 percent of the total slag volume and were not consistently found among the slag samples.



**FIGURE 2** Backscattered electron images of steel slags: (a) Slag D interior, (b) Slag D interface, (c) Slag F interior, (d) Slag F interface.

Table 2(a) also shows that the interface regions (edge areas) were very different in composition. These regions exhibited more variation in composition than the two “bulk” phases but were primarily calcium-rich. As seen in Figure 2(b), these interface regions were quite thick, extending more than 100  $\mu\text{m}$  into the interior of the slag particle. However, these regions were not uniformly distributed around the perimeter of the slag particles; for most samples, this type of nonhomogeneous outer layer made up between 20 and 80 percent of the total perimeter of the particle. This means that the surface reactivity of the slag will be controlled in part by the phases present in this layer. Some of the data, in particular the results from Slag E, Table 2(b), also indicated detection of chlorine in the outer interface region, further suggesting that this layer is reactive and sensitive to environmental conditions.

Slag F was the only slag sample that did not exhibit this nonuniform layer at the outer surface, [Figure 2(c,d)]. It is unclear why this slag should exhibit surface features different from the other samples examined, although it was the only EAF slag in this study. The microprobe data on this slag [Table 2(c)] also indicated that the

light-colored phase (the mixed oxide phase) was lower in iron oxide and higher in MgO component compared with the BOF slags.

### Chemical Composition of Steel Slags

Results of the chemical analysis and free lime content of the slags are given in Table 3(a); the physical properties for the aggregates are given in Table 3(b). Results indicate that all the BOF slags have very similar chemical composition. EAF Slag F has a lower iron oxide content and free lime content compared with the other slags.

### Moisture Uptake and Expansion Test Results

#### Moisture Uptake

The percentage mass increases for the different steel slag fine aggregates under different relative humidities are given in Figure 3, which

TABLE 3 Steel Slag Properties: (a) Chemical and (b) Physical

(a) Component %wt.	Slag Type				
	A	B	C	D	F
% Insoluble	11.9	13.7	12.9	10.5	14.2
Fe <sub>2</sub> O <sub>3</sub>	26.4	23.2	19.6	28.9	18.5
Al <sub>2</sub> O <sub>3</sub>	7.85	11.4	8.0	4.5	15.8
CaO	45.3	44.5	44.5	41.5	45.3
MgO	9.95	6.9	10.5	11.2	3.6
Heat Loss	-1.5	-0.03	1.1	3.1	2.2
Free Lime	4.15	3.0	3.8	4.7	1.1

(b) Properties	Slag Type			
	A	B	D	F
Polished Stone Value (PSV)	60.5	61.0	63.0	61.0
Aggregate Abrasion Value (AAV)	3.6	3.5	4.2	—
Absorption	1.195	1.438	2.535	1.9
Relative Density, Bulk	3.417	3.36	3.28	3.194
Relative Density, Apparent	3.565	3.53	3.577	3.401
Wash Pass 75 $\mu$ m	2.98	3.85	4.35	6.36

indicates that rate of moisture uptake is strongly dependent on relative humidity. Higher water uptake of Slag D is probably caused by relatively less abundance of well-formed crystal phases in this slag compared with other slags, a result of cooling rate differences.

#### Expansion Test

Results obtained for Slags A, D, F, and trap rock samples are given in Figure 4. All the slags used in this test showed volume expansion in excess of 1 percent in 1 week, which is the maximum permissible expansion recommended for highway construction materials (aggregate and fill materials). However EAF Slag F and Slag A (an experimental BOF slag) showed lower percentage expansion compared with the other two slags. These results also show that volume expansion does not necessarily correspond to the free lime content of the samples.

The HMA expansion test conducted by immersing the briquettes in water for 24 hr at 60°C revealed that all the briquettes prepared with Slags A and D also failed because of high volume expansion, which indicates that expansivity from moisture uptake/reactivity is too large to meet proposed draft specifications.

#### Accelerated Weathering Experiments

##### Slag Particle Results

In the first set of slag particle experiments it was observed that high humidity exposures at 30°C resulted in a change in surface

morphology. These results show that during exposure, the surface of the slag became covered in a thick crystal-like deposit. As shown in Table 4, this change in surface morphology was accompanied by an increase in calcium levels of the surface compared with initial surface composition, given in Table 1. These calcium-rich crystals were easily removed from the surface and easily fractured. Such "weathering" products would obviously be undesirable as an interface layer for wetting with asphalt because of their fragility. These surface deposits were first observed after 10 days at 30°C. As shown in Table 4, longer exposures did not seem to change the composition of the surface deposits. This surface deposition was observed for all slags examined. The EDX spectrum obtained after aging is consistent with the presence of a calcium carbonate-type compound.

The changes in surface morphology of the slag particles after exposures to 100 percent RH at 50°C were very similar to the results obtained at 30°C. The main difference, as expected, was the rate at which surface deposits formed. As shown in Table 4, these deposits were higher in calcium. This is probably because the 50°C deposits were more uniform and thicker than the 30°C deposits, resulting in more signal from the surface layer in the former case and more signal from the underlying substrate in the latter case.

##### Steel Slag Marshall Briquette Results

The slag/asphalt interface before exposure was characterized by uniform coverage of aggregates with asphalt with no sign of deposits and all internal voids free of debris. After exposure periods

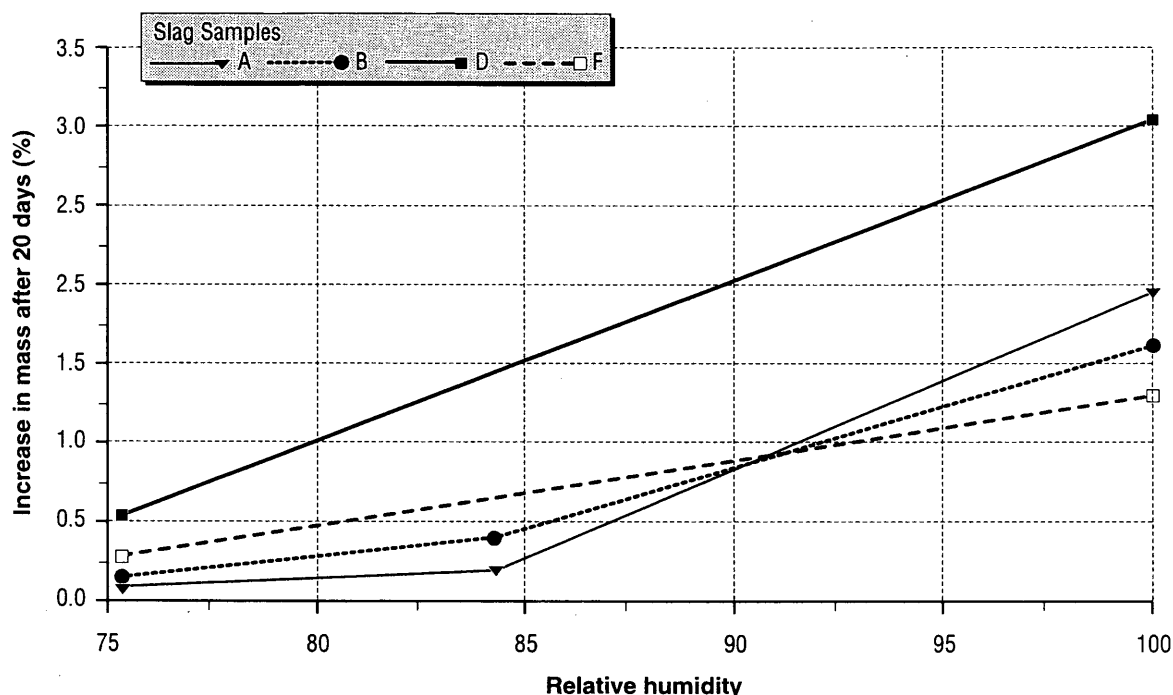


FIGURE 3 Moisture uptake of steel slags at different relative humidities.

of only 10 days at 50°C there were signs of deposits on all the exposed slag faces. These deposits were uniformly distributed across the slag surfaces and, as determined by the EDX analysis, were also calcium-rich. All the slag briquette samples examined exhibited this growth of calcium-rich material on the exposed slag surfaces. At longer exposure times, it was observed that internal voids and cracks were also becoming filled with this white crys-

talline deposit. It seems the calcium-rich crystals were able to form wherever a moisture film was present. This concurs with the assumption that the thin film of moisture in contact with exposed slag faces would become saturated with dissolution products from the slag. These dissolution products would then be free to move in the water phase to other locations; hence deposition would also occur within these cracks and pores.

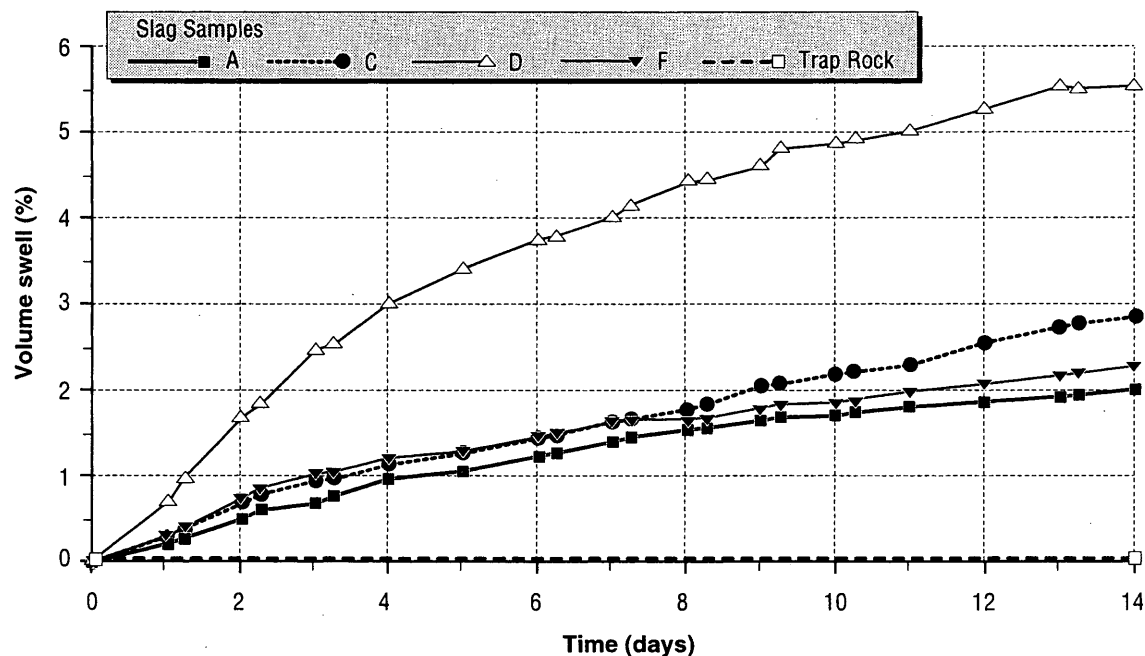


FIGURE 4 Steel slag aggregate expansion test results.



TABLE 4 Composition of Steel Slag Surfaces After Aging at 100 Percent RH as determined by EDX Analysis

Slag	Time Aged (d)	Temp. (°C)	Element (wt%)							
			Ca	Fe	Al	Si	Mg	Mn	C	O
A	10	30	48.0	0.0	0.0	0.6	0.0	0.0	10.0	41.0
	45	30	53.0	0.0	0.0	0.0	0.0	0.0	9.1	38.0
	10	50	67.0	0.0	0.0	0.8	0.0	0.0	11.0	21.0
B	10	30	45.0	0.0	0.0	0.0	0.0	0.0	7.9	47.0
	45	30	51.0	0.0	0.0	0.0	0.0	0.0	8.9	40.0
	10	50	75.0	0.0	0.0	0.0	0.0	0.0	4.3	21.0
C - Area 1	10	30	52.0	0.0	0.0	0.0	0.0	0.0	11.0	37.0
	45	30	55.0	0.0	0.0	1.0	0.0	0.0	10.0	34.0
	10	50	72.0	0.0	0.0	0.0	0.0	0.0	3.8	23.0
C - Area 2	10	50	34.0	0.0	0.0	0.3	0.0	0.0	19.0	48.0
D	10	30	51.0	0.0	0.0	1.0	0.0	0.0	12.0	36.0
	45	30	55.0	0.0	0.0	1.3	0.0	0.0	13.0	31.0
	10	50	71.0	0.0	0.0	1.2	0.0	0.0	8.9	19.0

These calcium-rich deposits were also observed on the top (uncut) surfaces of the briquettes wherever slag particles were present, either uncovered or only partially covered by the asphalt.

In many of the briquette samples, cracks formed after prolonged exposures (>1 month) at 50°C. The path of these cracks often progressed along the slag-asphalt interfaces, and calcium-rich deposits formed in many of the cracks. The expansion test and FT-IR results suggest that the cracks were formed because of changes in the slag volume rather than changes in the asphalt characteristics. Cracks were observed in all slag briquette samples.

The only briquette samples not exhibiting aggregate reactions (and, interestingly, no visible cracks after humidity exposures) were the briquettes made with traprock. Even after 3 months at 50°C, the aggregate-asphalt interface appeared uniform and free of defects, and all internal voids were free of deposits.

Good field core samples were characterized by slag-asphalt interfaces that appeared uniform with good adhesion and coverage, as shown in Figure 5(a). Also, these cross sections exhibited internal voids that were free of debris. In contrast, the cross sections of field cores that were described as having poor behavior (many cracks) exhibited slag-asphalt interfaces that had accumulated white deposits. The internal voids of these poorly behaving field cores were also filled with this white deposit (Figure 5(b)). EDX analysis confirmed that the deposits were very similar in composition to the surface deposits found on the briquette samples after aging.

Experiments in which cross sections of field cores were placed in the humidity chamber at 50°C also showed that both good and bad field cores exhibited some slag surface reactivity with calcium-rich deposits forming as shown in Figures 5(c) and (d). This clearly indicates that contact with moisture can still result in a reaction with the steel slag, even after it has been in service for many years, suggesting that the reactivity is probably due to the hydratable phases in steel slag, mainly the calcium silicate phase.

### FT-IR Results

Samples were prepared in a manner similar to that described previously (8). Numerous samples of the asphalt were obtained from the interface and near-interface regions and were characterized using diffuse-reflectance FT-IR. Particular emphasis was placed on the carbonyl region (1690 to 1850 cm<sup>-1</sup>), where it has been demonstrated previously that changes caused by asphalt oxidation can be observed.

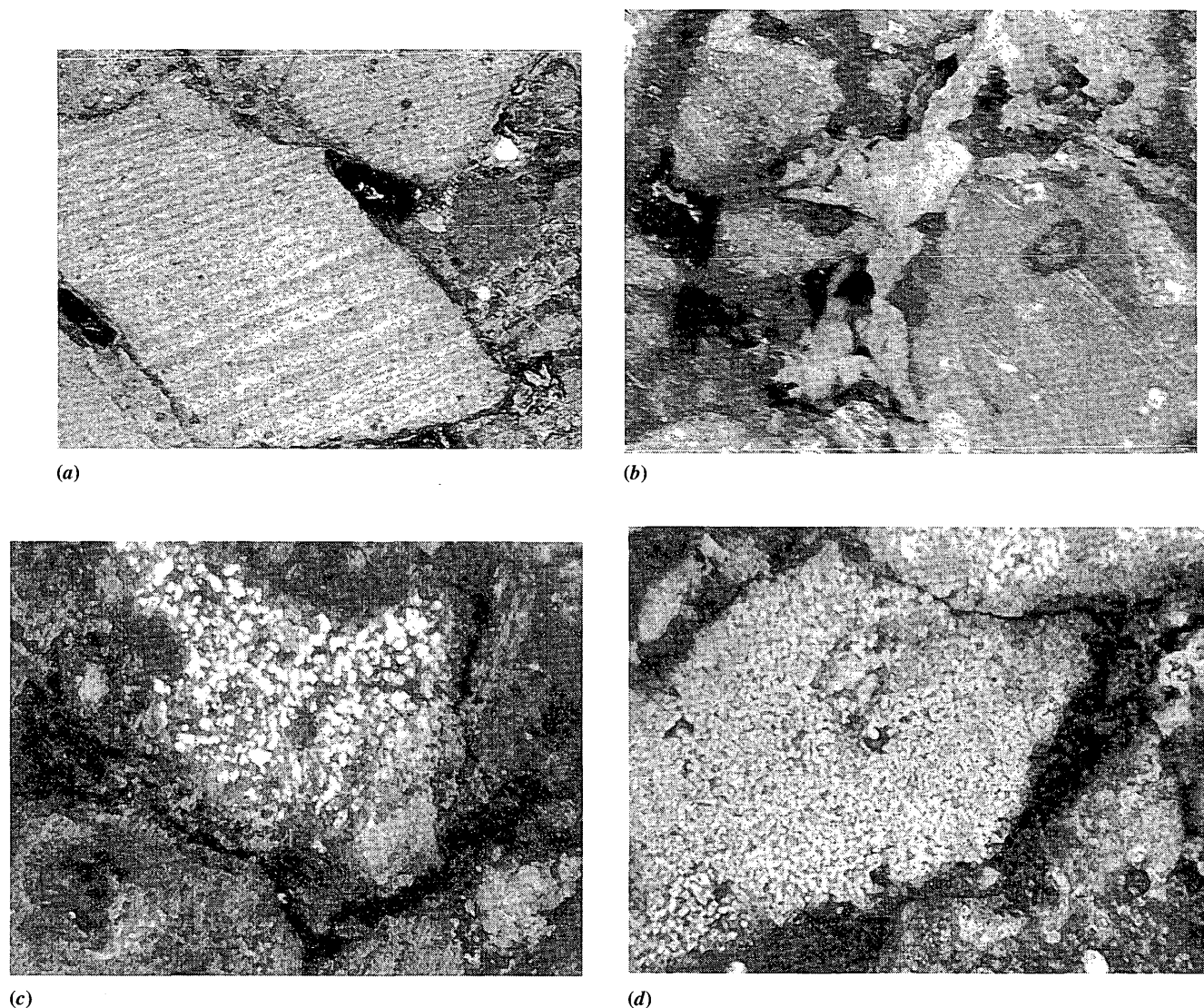
Although changes were observed in the slag-asphalt interface after these weathering experiments, these did not relate to any systematic changes in the FT-IR response. In particular, no significant changes were observed in the carbonyl region of the spectrum.

### Mineralogical Characterization by XRD

To summarize the major findings of the XRD analysis, the predominant mineral phases found can be separated into five categories (12): (a) wuestite (FeO); (b) calcium silicates (Ca<sub>3</sub>SiO<sub>5</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, β-Ca<sub>2</sub>SiO<sub>4</sub> (larnite), and Ca<sub>54</sub>MgAl<sub>3</sub>Si<sub>16</sub>O<sub>90</sub>); (c) calcium oxides and ferrites (Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, CaFeO<sub>2</sub>, CaFe<sub>3</sub>O<sub>5</sub>, and CaO); (d) manganese oxides ((Mn,Mg)(Mn,Fe)<sub>2</sub>O<sub>4</sub> (hausmannite)); and (e) periclase (MgO).

The microprobe analysis indicated that the two predominant phases were a mixed oxide phase consisting of FeO, MnO, and MgO along with varying low levels of CaO and a CaO/SiO<sub>2</sub>-rich phase. This first phase would be expected to exhibit contributions to the XRD pattern from the FeO, MgO, MnO components as well as from hausmannite. The other dominant phase observed in the cross-sectional analysis, the CaO/SiO<sub>2</sub>-rich phase, could be anything from the various calcium silicate minerals listed in the preceding paragraph, but the ratio Ca/Si as determined by the micro-





**FIGURE 5** Optical micrographs of steel slag-asphalt field cores: (a) cross section of "good" field core, (b) cross section of "poor" field core, (c) "good" field core after aging (10 days at 50°C, 100 percent RH), (d) "poor" field core after aging (10 days at 50°C, 100 percent RH).

probe would indicate that it was predominantly in the form of a  $\text{Ca}_2\text{SiO}_4$ -like phase.

The XRD data indicated the presence of far more mineral phases than were implied by the microprobe analysis. This may be because the XRD data were generated from crushed bulk samples. Whereas the microprobe data were generated from discrete phase fields that may have varying composition on a local scale that was not analyzed, the XRD data were able to differentiate among the many phases present.

The mineralogical information of steel slag can also be used to examine some of the possible reactions that may occur when these materials are exposed to the accelerated weathering conditions. Some of the possible reactions involve the calcium silicates hydrating to form C-S-H gels as in portland cement or the calcium oxides forming portlandite ( $\text{Ca}(\text{OH})_2$ ) and goethite ( $\text{FeO}(\text{OH})$ ). Instability of steel slags has been attributed to the existence of bicalcium silicate in  $\beta$ -metastable form and the presence of free lime (13). The periclase may also be expected to hydrate and form brucite

( $\text{Mg}(\text{OH})_2$ ). With the presence of  $\text{CO}_2$  in the moisture on the slag surface, there would be further formation of calcium carbonate ( $\text{CaCO}_3$ ) from the calcium hydroxide species present.

The results obtained from both the SEM/EDX analysis of the deposits on the slag surfaces after weathering and from the slag-asphalt interface, both in-service and after weathering, show that the formation of calcium carbonate is the main reaction. From the phases present, the most likely source of the calcium would be the various calcium silicate phases detected in the slag cross sections. Another source of calcium would be the calcium-rich layer found in regions at the outer surface of many of the slag samples examined.

## DISCUSSION OF RESULTS

This study has shown interesting results about the behavior of steel slags in contact with moisture. All slag samples examined exhibited formation of calcium-rich deposits (mainly calcium carbonate),

even after a relatively short exposure of 10 days at 30°C at 90 to 100 percent RH. Steel slags in asphalt briquettes also exhibited calcium-rich deposits. In many cases, cracks were observed in the briquette cross sections after aging; the path for these cracks was often along slag-asphalt interfaces that exhibited deposit formation, indicating that asphalt-steel slag bond failure had occurred.

The appearance of the slag-asphalt interface after the accelerated aging experiments was similar to the interfaces from field cores obtained from steel slag-asphalt pavements in service for several years. The deposits formed after the accelerated aging experiments were very brittle and fragile and loosely attached to the surface. The aggregate expansion test and HMA expansion test results showed substantial volume increases caused by this reactivity of the steel slags samples with moisture, a cause of premature cracking and failure.

The main concern is still the general moisture reactivity and expansivity exhibited by all the steel slag samples examined. Although the free lime content of some samples was low, the slags reacted with moisture to form calcium-rich deposits. This also indicates that even with low unreacted lime content, generally considered the main cause of swelling and premature failure at the slag-asphalt interface, if moisture is allowed to enter the system there is potential for further deterioration of the slag-asphalt bond as the moisture interacts with the steel slag. Indeed, exposure of both good and bad field core cross section samples to the humidity tests confirmed this reactivity.

There are two implications of this surface reactivity: (a) the ingress of moisture to the interface can displace asphalt from the interface because the slag surface is more hydrophilic than asphalt and (b) the fragile surface deposits that form on the steel slag during exposure to moisture may weaken the strength of the asphalt-aggregate interface. Thus, the situation may degrade both the mechanical and chemical aspects of the aggregate-asphalt bonds (14).

In contrast, traprock briquette samples did not exhibit the same degree of reaction with moisture. No surface deposits were observed on the aggregate surfaces, the aggregate-asphalt interface remained intact, and cracking did not occur.

The examination of prepared cross sections by EPMA and XRD analysis of bulk samples indicated that the mineralogy of the steel slags was very complex. Although there appeared to be consistency in the types of phases present, there was much variability in phase distribution in the bulk of the slag particles. The main cause of these differences is thought to be the cooling rate, which affects the mineralogy and surface characteristics and, to a lesser extent, changes in steel-making practice that determine the bulk chemistry of steel slags; batch operations also introduce variability. Also, composition of the surface zones was different from that of the bulk of the slag particles. Oxide phases based on FeO, MnO, MgO, and CaO and calcium silicate phases were predominant. XRD analysis indicated little difference in phase composition as a function of particle size. The primary source of the calcium-rich deposits formed during aging experiments appears to be the calcium silicate phases and, to a lesser extent, the mixed oxide phase containing calcium oxide. This study suggests that control of the amount and distribution of these types of phases may be a way to control the inherent reactivity of steel slag in moist environments.

Water uptake and expansion tests examine the behavior of steel slag and steel slag-asphalt mixes on a macroscopic level and should always be used to screen slag materials for potential application as aggregate. However, if the reduction in unreacted lime and the asso-

ciated expansion characteristics do not prove to be the sole predictor of steel slag behavior in asphalt mixes, then a detailed study may be necessary to further optimize steel slag chemistry. The combination of EPMA examination of prepared cross sections and XRD analysis has proved effective in characterizing steel slags.

## CONCLUSIONS

1. All steel slag samples used in this study exhibited surface reactivity during high humidity weathering experiments. This reactivity resulted in the formation of white crystalline surface deposits of a calcium carbonate-like compound.

2. During high-humidity exposures, steel slag briquettes also developed white deposits. In some cases cracking developed along slag-asphalt interfaces.

3. Examination of field cores indicated that slag-asphalt interfaces were characterized by the presence of white deposits containing mainly  $\text{CaCO}_3$ , which were similar in composition to those found in the laboratory weathering exposures.

4. Mineralogical characterization indicated that steel slags exhibited similar bulk phase composition, but the distribution (microstructure) of the slags was very different. In most cases, outer surface regions of the slag were of different composition from the slag interior. The main phases present were oxide phases based on FeO, MnO, MgO, and CaO, and calcium silicate phases. The most likely source for the calcium-rich deposits formed during humidity exposures are the calcium silicate phases present in the slags.

5. All steel slag aggregate samples showed volume expansion excessive of proposed draft specifications for aggregates in highway construction. However, BOF experimental slags studied showed reduced expansivity compared to a typical production sample, indicating that suitable processing methods may control volume expansivity of steel slags.

6. The failure mechanism observed in steel slag aggregate mixtures was attributed mainly to the excessive expansivity of steel slags due to reaction with moisture. This reactivity could be the cause of long-term degradation of the asphalt-aggregate interface in the presence of moisture.

## RECOMMENDATION

The relationship between steel slag phase distribution, processing parameters (such as cooling rates), and their effects on reactivity and expansivity of steel slags should be investigated with a view to producing high quality aggregate for highway construction. This study may be extended to include modification of steel slags with other materials.

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