

# Characterization of Base and Subbase Iron and Steel Slag Aggregates Causing Deposition of Calcareous Tufa in Drains

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Tufaceouslike materials are observed clogging pavement drains along highways in northeastern Ohio. These materials have also been found in catch basins and spillways. Previous studies suggest that the original free lime (CaO) in slags used as subbase materials is responsible for the deposition of the tufa. To characterize these slags, X-ray diffraction, energy dispersive X-ray, surface area measurements, CaO solubility in anhydrous ethylene glycol ("sugar test"), and other physicochemical tests were conducted on air-cooled blast furnace (ACBF), open-hearth (OH), and basic oxygen furnace (BOF) slags. ACBF iron slag is composed of crystalline akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ). Results of the sugar test indicate that this slag does not contain any residual or easily available free lime. The ACBF sample exhibited the lowest surface area and therefore is the least reactive with  $\text{CO}_2$ -charged waters. The OH and BOF slags, however, exhibit the presence of CaO or its weathering equivalents such as  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ . All these steel slags exhibit a high tufa-generating potential. Analysis of the physicochemical tests of these steel slags indicates that they are composed mainly of  $\beta$ -dicalcium silicate (larnite), calcium ferrites, wüstite (FeO), free lime (CaO), periclase (MgO), portlandite [ $\text{Ca}(\text{OH})_2$ ], and calcite ( $\text{CaCO}_3$ ). These slags also exhibit high surface areas and are more reactive with  $\text{CO}_2$ -charged waters. Most highway departments require that steel slags be aged or cured for at least 6 months before they are used. Sugar tests conducted on samples obtained from different horizontal depths (up to 10 ft) in a stockpile showed that the CaO (free lime) content increases with increasing depth into the stockpile. Evidently some of the free lime is encapsulated by insoluble silicates or is in occluded pores and has not come in contact with  $\text{CO}_2$ -charged porewater. Therefore, aging of slags by exposure to weathering does not necessarily decrease the free lime content enough to prevent the formation of tufa. It is concluded that the presence of CaO, MgO,  $\text{Ca}(\text{OH})_2$ , and  $\text{CaCO}_3$  in slags is critical in determining their tufa potential for use as base and subbase aggregates.

Iron and steel slags have been used as base and subbase aggregates in several northeastern Ohio pavement construction projects. Along these highways, tufaceouslike materials have been observed clogging many subdrains (1). These materials have also been found in catch basins and spillways. Some of the drain outlets have been observed completely clogged with tufa, creating water retention and soft-pavement conditions. Furthermore, frost action on the retained water results in severe distresses that also cause premature failure of the pavement. Tufa deposition in these pavement structures, therefore, leads to early pavement deterioration and costly maintenance.

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The main component of tufaceous precipitates is calcium carbonate. It is termed *tufa* because it is similar to deposits that occur in natural systems. Bates and Jackson (2) define tufa as a natural chemical sedimentary rock composed of calcium carbonate formed as precipitate by the evaporation of natural water rich in dissolved calcium carbonate. Research studies (3,4) have suggested that free lime (CaO) in these slags is responsible for producing tufa.

## FORMATION OF TUFA

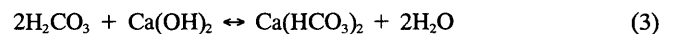
The chemical reactions between free lime and rainwater occur under the pavement surface. The free lime reacts with rainwater and forms calcium hydroxide  $\text{Ca}(\text{OH})_2$  in pavement drains. The formation of tufa from free lime is explained by the following chemical reaction:



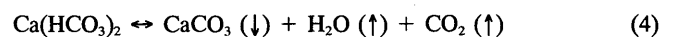
The calcium hydroxide solution in the drain water produces pH values of more than 11.0. Also, high concentrations of carbon dioxide from the atmosphere and automobile exhaust react with rainwater forming carbonic acid ( $\text{H}_2\text{CO}_3$ ):



The carbonic acid reacts with calcium hydroxide forming calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ], which is more soluble in water than  $\text{CaCO}_3$ .



At the orifices of drains and in catch basins, the water from this enriched solution of calcium bicarbonate evaporates because of warm temperatures, and the carbon dioxide escapes into the atmosphere. This condition leads to the precipitation of calcium carbonate and the formation of tufa:



Warm temperatures lead to increased rates of deposition of tufa, whereas at cold temperatures the  $\text{CO}_2$  remains in solution and favors dissolution. These conditions lead to increased tufa precipitation during the summer months and less precipitation during

the winter months. These chemical reactions clearly indicate that the concentration of free lime, water, carbon dioxide, temperature, and humidity are the main elements that control the precipitation of tufaceous deposits in drains and catchment basins of highways.

## SCOPE OF PAPER

The objective of this research is to study the physicochemical properties of tufa and iron and steel slags. In pursuit of this objective, various laboratory experiments were conducted to determine the tufa-producing potential of the slags. The tufa and slag samples are described in this paper, as well as the laboratory experiments. Research findings and conclusions are presented with regard to the potential use of steel slags.

## TUFA AND SLAG SAMPLES

### Tufa Samples

A field trip was arranged through Ohio Department of Transportation (ODOT) to collect tufa samples from different locations in which slags were used as subbase aggregates. Five tufa samples were obtained from different locations in Cuyahoga County where pavement subdrains were clogged by tufa. Site investigation revealed that different types of slag had been used as the subbase aggregate at each site. At these sites, tufa was observed to be clogging drains 5 to 6 years after the original emplacement of the pavement.

### Slag Samples

Eight 80- to 100-lb slag samples were provided by ODOT. These samples consisted of one aged air-cooled blast furnace (ACBF) slag, three aged open-hearth (OH) slags, and four basic oxygen furnace (BOF) slags (two aged and two unaged). The aged samples were from the stockpiles exposed to the atmosphere for more than 6 months. The actual period of aging, however, was not known. The unaged samples were from either fresh stockpiles or stockpiles stored for less than 3 months.

## LABORATORY STUDIES

### Chemical and X-ray Diffraction Analyses of Tufa Samples

Pure tufa contains only calcium carbonate, but the tufa samples obtained from the field contained some impurities such as organic matter, quartz, and elements leached out from the slag aggregate. The chemical analysis included the removal of organic materials by hydrogen peroxide (30 percent) oxidation, determination of the percent insoluble residue (ISR), calcium carbonate,  $R_2O_3$  (oxides of Al, Fe, Mn, and P), and loss on ignition (LOI).

Table 1 shows the results of the chemical analysis on these tufa samples, including the organic matter content, which varies from 0.67 to 1.06 percent; the  $R_2O_3$  content, which varies from 4.0 to 14.0 percent; and the LOI, which varies from 35 to 42 percent. These LOI values mostly correspond to the loss of carbon dioxide on heating the tufa. In Sample 1 the calcium carbonate content is 84.75 percent and the corresponding LOI is 37.30 percent as compared with 44 percent for pure calcium carbonate. The same is true for all other tufa samples. The main component in all tufa samples therefore is calcium carbonate regardless of the steel slag used as a base or subbase material. Insoluble residue values varied from 0.53 to 8.24 percent. These are due mainly to the insoluble impurities such as quartz or possibly clays. X-ray diffraction of the tufa samples verified the results of the chemical analysis. Figure 1 shows the X-ray diffractograms of the tufa samples. These diffractograms show that the tufa markedly consists of calcite ( $CaCO_3$ ), quartz ( $SiO_2$ ), and minor amounts of dolomite [ $(Ca,Mg)(CO_3)_2$ ]. The dolomite most likely is a contaminant derived from the dolomitic aggregate in the concrete.

### Oxide Analysis of Slags

The oxide analysis provided the percentage of the elements as oxides present in the slag samples. This analysis was done in accordance with ASTM E886-88, a procedure to identify elements such as aluminum, calcium, iron, magnesium, phosphorus, potassium, silicon, sodium, and sulfur by X-ray fluorescence (XRF) methods. ASTM procedures E790 and C114-16.2 were used also to identify the moisture content and LOI, respectively.

Table 2 shows the results of oxide analysis of the slag samples. The dominant element in the slags as an oxide is calcium. The next two most abundant oxides are those of silicon and iron. Oxides of calcium in the OH slags vary from 34 to 41 percent,

TABLE 1 Chemical Analysis of Tufa Samples (Values in Percentages)

Sample Number	Organic Matter	ISR <sup>a</sup>	R <sub>2</sub> O <sub>3</sub> <sup>b</sup>	CaCO <sub>3</sub> <sup>c</sup>	Total Percent	LOI <sup>d</sup>
1	0.91	8.24	6.10	84.75	100	37.30
2	0.86	3.50	9.60	86.04	100	36.67
3	0.67	0.53	4.23	94.57	100	41.67
4	0.76	5.40	13.37	80.47	100	35.47
5	1.06	0.55	4.80	93.59	100	41.37

a - Insoluble Residue

b - Could be Fe, Al, Mg, P, or Mn

c - Calcium Carbonate

d - Loss On Ignition

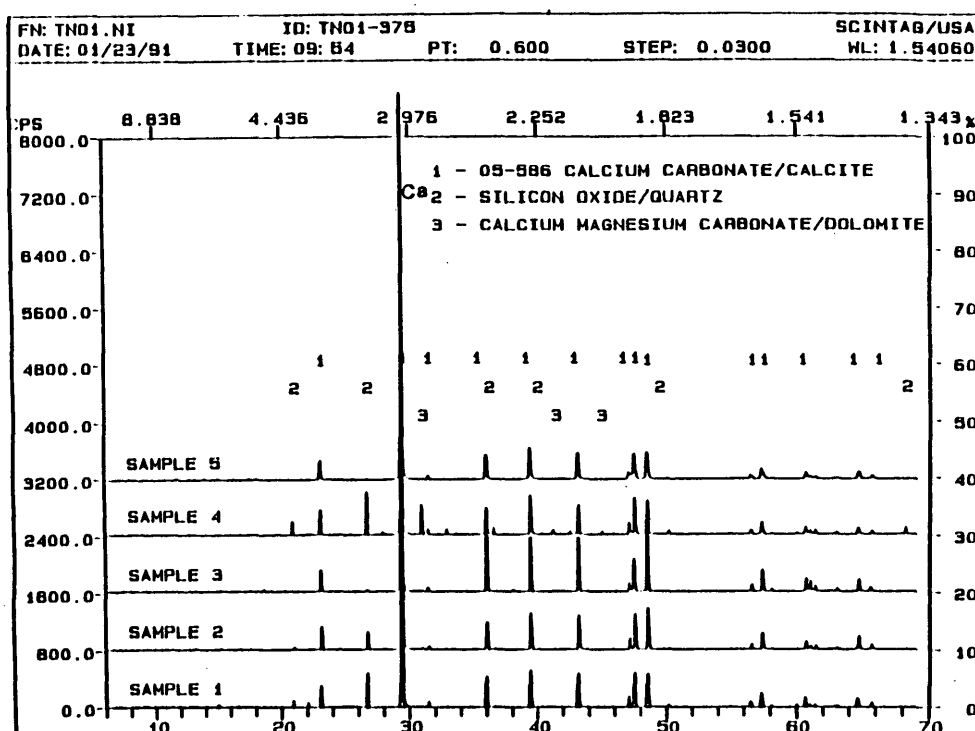


FIGURE 1 X-ray diffractograms of tufa Samples 1 to 5.

whereas in the BOF slags, it varies from 35 to 51 percent. The ACBF slag contains about 40 percent oxides of calcium and has the highest silica content (38 percent), whereas the silica content in other slags varies from 15 to 25 percent. Furthermore, the ACBF slag has the highest content of aluminum and magnesium and the least percentage of oxides of iron as compared with other slags. Table 2 shows that the ACBF slag does not contain any measurable LOI, which indicates that no carbonates are present. The OH and BOF slags contain aluminum (3 to 4.5 percent), iron (15 to 25 percent), magnesium (5 to 9.5 percent), and manganese (2 to 5 percent). These slags contain carbonates, as indicated by their LOIs, which range from 1.5 to 10.5 percent. All samples contain minor amounts of oxides of phosphorus, potassium, sulfur, and sodium and contain trace amounts of oxides of strontium, barium, chromium, and vanadium.

The data in Table 2 help to identify various chemical and mineral phases present in the slags during the X-ray analysis. It is

noteworthy that the calcium oxide content shown in Table 2 is the total possible calcium oxide inclusive of any free lime in the slags.

### X-Ray Diffraction Analysis

X-ray powder diffraction analysis determined the gross mineralogy of the slags. Oven-dried slag samples (between -275 and +325 sieve size) were used in the X-ray diffraction analyses. All powder diffraction data were accrued using SCINTAG Powder Diffractometer XDS2000, with a Cu tube operated at 45 kV and 40 mA. A high-purity solid-state germanium (HPGE) detector cooled by liquid nitrogen was also used. The SCINTAG software package (DMS 2000 version 1.88 with JCPDS data base version .40) was employed for all calculations carried out on a Micro Vax 3100 computer. The diffraction patterns for all samples were recorded by continuous scan at a scanning speed of 3 degrees/min

TABLE 2 Oxide Analysis of Slag Samples

Sample #	Slag Type	Oxides											LOI	Oth <sup>a</sup>
		Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	SO <sub>2</sub>	Moisture		
1	ACBF	8.52	40.09	0.85	10.80	0.71	0.02	0.24	38.09	0.23	0.24	0.04	-	0.2
2	OH	3.50	36.02	26.57	9.84	3.31	0.26	0.01	15.19	0.06	1.70	0.42	3.1	-
3	OH	3.57	40.76	23.81	7.81	5.26	0.10	0.01	13.73	0.01	0.01	0.78	1.5	1.1
4	OH	4.66	34.02	15.41	5.04	3.39	0.10	0.17	26.06	0.08	0.01	0.57	10.5	-
5	BOF	3.75	35.27	24.08	10.52	2.81	0.29	0.01	12.77	0.08	0.01	3.08	5.5	1.8
6	BOF	4.46	38.49	26.33	8.35	4.48	0.13	0.01	12.41	0.07	0.01	0.61	2.1	2.5
7	BOF	2.97	48.02	15.05	9.67	3.12	0.22	0.01	13.21	0.01	0.01	1.65	6.1	-
8	BOF	3.01	50.81	15.62	5.32	3.56	0.30	0.01	15.04	0.01	0.04	2.88	3.4	-

<sup>a</sup> Oth - Others commonly include SrO, BaO, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>

with a "step size" of 0.03 degree/min. Search-and-match routines were used against the JCPDS data base for the identification of the resulting peaks. The search was limited to the elements H, Na, K, Mg, Ca, Al, Fe, C, Si, P, N, S, O, and Cl. The peaks below 5 percent of relative intensity were not taken into account for the preliminary search. The solution was accepted if it fell into the error window of 0.3 percent of a given d-spacing. Because the samples were weathered, many secondary minerals can occur concomitantly with the primary slag minerals. This condition creates a sample composed of multiphases and produces overlapping peaks on the diffractograms. Therefore, some of the mineral species in Table 3 may be spurious. To decrease this spurious tendency, the minerals in Table 3 were verified by petrographic analysis using a polarizing light microscope in both the transmission and reflection modes. Those minerals that were verified by petrographic polarizing microscope are indicated by a footnote in Table 3. In addition, those minerals in Table 3 that are not footnoted have been known to occur in slags.

X-ray diffractograms of ACBF slag (Figure 2) show that akermanite and an unnamed mineral (Fe-Mg-Al-SiO) occur as the major phases. Other compounds such as rhodochrosite, mackinawite, iron calcium sulfide carbonate hydrate, and an unnamed mineral are present as minor or trace phases. Some of these phases may be artifacts induced by overlapping. Figure 3 shows the X-ray diffractograms for three OH slag samples. In all the samples, silica, mayenite, augite, hematite, magnesite, and gehlenite are present as major phases. Other compounds and minerals are present in trace amounts.

Figure 4 shows the X-ray diffractograms of the BOF slag samples. Comparison of all the BOF slag samples indicates that Samples 5 and 6 contain silica, grossular, magnesium calcium carbonates, calcium iron oxide (ferrite), and portlandite  $\text{Ca}(\text{OH})_2$ , whereas slag Samples 7 and 8 contain larnite ( $\beta\text{-Ca}_2\text{SiO}_4$ ), portlandite [ $\text{Ca}(\text{OH})_2$ ], wüstite (FeO), and clinoferrosilite ( $\text{FeSiO}_3$ ) as major phases. Other possible compounds in the BOF slags occur as minor phases: iron oxides, ferrites, phosphates, silicates, and sulfides.

Various mineralogical phases are identified by a computer search match for the slag samples. Approximately 50 different species were identified by the computer search match in all the samples. The 50 mineral species are grouped into 6 major mineral types (see Table 3): silicates, oxides and hydroxides, carbonates, phosphates, sulfides, and chlorides. These species are further identified according to their relative abundances as A for presence in abundance, P for present but in less quantity, M for presence in minor quantity, and T for presence as a trace.

The most important mineralogical phases for this research study are the presence of calcite ( $\text{CaCO}_3$ ), perclase ( $\text{MgO}$ ), or portlandite [ $\text{Ca}(\text{OH})_2$ ] in the slag samples because they can increase the tufa precipitate potential. In OH slag Sample 2, both calcite and portlandite occur, whereas OH slag Sample 4 contains only calcite. The OH samples have been exposed to weathering for as long as 80 years and at least for 15 years. The latter estimate of exposure is based on the fact that 1978 was the last year that OH slag was generated. Apparently all the CaO and  $\text{Ca}(\text{OH})_2$  in Sample 4 has been totally carbonated. The BOF slag Samples 5, 7, and 8 contain both portlandite and calcite except for Sample 6, which contains only calcite. Again this depends on the degree of exposure to the atmosphere. Thus the OH and BOF slags exhibit a higher potential for producing tufa. The time required and the volume of tufa precipitate may vary among slag types depending on many factors:

reactivity of slags, surface area, particle size, pore size distribution, amount of water, absorption, and so on.

ACBF slag does not contain either calcite or portlandite. It consists mainly of calcium magnesium aluminum iron silicates. In the past, ACBF slags have exhibited the most inertness of all aggregates and therefore should not produce any tufa. This statement is reinforced strongly by the absence of mineral species responsible for tufa precipitation.

### Surface Area Measurements

The surface area of a material controls the rate of chemical reaction between solids and gases or liquids. The surface area measurements of the slag samples were conducted to differentiate the relative reactivity of these slags. From knowledge of the surface area measurements and mass percentage of the total reactive free lime in the slag, it is possible to predict their tufa potential properties.

Surface area (SA) measurements using slags sized between -275 and +325 mesh were made on a micromeritics Gemini 2360 Analyzer, which is fast and simple to operate. The units of measurement are named after the authors who developed the procedures and formulas to calculate SA measurements of solids. The Brunauer, Emmett, and Teller (BET) method calculates multipoint and single-point SAs, whereas the Langmuir method calculates multipoint SAs. Software coupled with the Gemini unit automatically generates reports and calculates the following: single-point BET SA, multipoint BET SA, multipoint Langmuir SA, and total pore volume. In addition, this instrument can report up to 1,000 discrete point adsorption isotherms. As many as 50 data points can be reported in the BET range and can be plotted on an X-Y recorder.

Gemini uses a flowing gas in which the analysis gas ( $\text{N}_2$ ) flows simultaneously into both the sample and balance tubes. The only difference between the two tubes is the presence of the sample in one of them. The delivery rate of the gas into the sample is controlled by the rate at which the sample can adsorb the gas onto the surface; the rate of flow into the balance tube is controlled to yield the same pressure. As the sample adsorbs the gas, the pressure tends to drop in the sample tube. A rapid servo-device continuously restores the pressure balance between the tubes by admitting more gas into the sample side. The result is that the unit maintains constant pressure over the sample while varying the rate of gas delivery to match the sample adsorption rate. Surface areas as low as 0.01  $\text{m}^2/\text{g}$  are easily determined with excellent precision using  $\text{N}_2$  gas as the adsorbate. Software accrues the data and calculates the SA according to the various methods mentioned above.

Table 4 gives the SA measurements for the slag samples. A comparison of the SAs among slags shows that OH slag Sample 3 has a larger SA than OH Samples 2 and 4. BOF slag Sample 7 has a larger SA as compared with Samples 5, 6, and 8. BOF slag Samples 5 and 8 have approximately same SA. BOF slag Sample 6 has the least SA and thus should produce less tufa as compared with the other BOF slags. This conclusion is drawn on the hypothesis that larger SAs will lead to a more rapid reaction. However, other factors, which include pore size distribution, effective porosity, degree of weathering, and total reactive free lime present in these aggregates, need to be considered to reach an accurate conclusion.

**TABLE 3 Results of X-Ray Diffraction Studies**

Mineral Type	Sample Number							
	1	2	3	4	5	6	7	8
<b>Silicates</b>								
Larnite ( $B Ca_2SiO_4$ ) <sup>a</sup>			P		A	A	A	A
Akermanite ( $Ca_2MgSi_2O_7$ ) <sup>a</sup>	A							
Hydro-Grossular ( $Ca_3Al_2(SiO_4)CO_3(OH)_3$ )	P				P	P		
Glaucochroite ( $(Ca,Mn)_2SiO_4$ )					T	T		
Wadsleyite ( $(Mg,Fe)_2SiO_4$ ) <sup>a</sup>						P		
Clinoferrosilite ( $FeSiO_3$ ) <sup>a</sup>							P	P
Fayalite ( $(Fe,Mg)_2SiO_4$ ) <sup>a</sup>							P	P
Nagelschmidite ( $2Ca_2SiO_4.Ca_3(PO_4)_2$ ) <sup>a</sup>								P
Pyroxene (Aluminium Augite) ( $Ca(Fe,Al,Mg)SiO_4$ )			A					
Gehlenite ( $(Ca_2Si)Al_2SiO_4$ ) <sup>a</sup>				A				
Unnamed (Fe-Mg-Al-SiO)	P		P					
Xonolite ( $Ca_6Si_6O_{17}(OH)_2$ )				T				
Goosecreekite ( $CaAl_2SiO_6.5H_2O$ )						P		
Calcio-Olivine ( $G Ca_2SiO_4$ ) <sup>a</sup>								M
<b>Oxides and Hydroxides</b>								
Periclase ( $MgO$ ) <sup>a</sup>		P			P		P	
Wustite ( $FeO$ ) <sup>a</sup>			P				P	
Hematite ( $Fe_2O_3$ ) <sup>a</sup>		M	M					
Magnetite ( $Fe_3O_4$ )				T				T
Hausmanite ( $(Mn,Mg)(Mn,Fe)_2O_4$ )		T		T		M		
Portlandite ( $Ca(OH)_2$ ) <sup>a</sup>		P	P	P	P	P	P	
Vernadite ( $Mn(OH)$ )					T			
Pyrochroite ( $Mn(OH)_2$ )					T			
Srebrodolskite ( $Ca_2Fe_2O_5$ ) <sup>a</sup>					A	A	A	A
Magnesioferrite ( $MgFe_2O_4$ )				T	T			P
Spinel ( $MgAl_2O_4$ )					T	P	M	
Mayenite ( $Ca_{12}Al_{14}O_{33}$ )		A	A					
Quartz ( $SiO_2$ )		T	M	M			M	
Moganite ( $SiO_2$ )								
Cristobillite ( $SiO_2$ )				T				
<b>Carbonates</b>								
Calcite ( $CaCO_3$ ) <sup>a</sup>		P		P	P		P	P
Magnesite ( $MgCO_3$ )					P			
Ferromagnesite ( $(Mg,Fe)CO_3$ )		M						
Dolomite ( $CaMg(CO_3)_2$ )			M				T	
Ferroan Dolomite ( $Ca(Mg_{0.67},Fe_{0.33})(CO_3)_2$ )							T	
Ankerite ( $Ca(Fe,Mg)(CO_3)_2$ )							T	
Rhodochrosite ( $MnCO_3$ )		T						
<b>Phosphates</b>								
Nagelschmidite ( $2Ca_2SiO_4.Ca_3(PO_4)_2$ ) <sup>a</sup>								P
Berlinite ( $AlPO_4$ )					P			
<b>Sulfides</b>								
Albandite ( $MnS$ )							T	
Hauerite ( $MnS_2$ )				T				
Pyrite ( $FeS_2$ )							T	M
Marcasite ( $FeS_2$ ) <sup>a</sup>								M
Mackinawite ( $((Fe,Ni)_9S_8)$ )		T						
Niningerite ( $MgS$ )			T					
<b>Chlorides</b>								
Halite ( $NaCl$ ) <sup>b</sup>					T			

A - Abundant, P - Partial, M - Minor, T - Traces

<sup>a</sup> - Presence verified by the petrographic polarizing microscope both in the transmission and the reflection modes.

<sup>b</sup> - Verified by energy dispersions X-ray analyses (EDS) and X-ray diffraction of the laboratory (leachate) produced tufa.

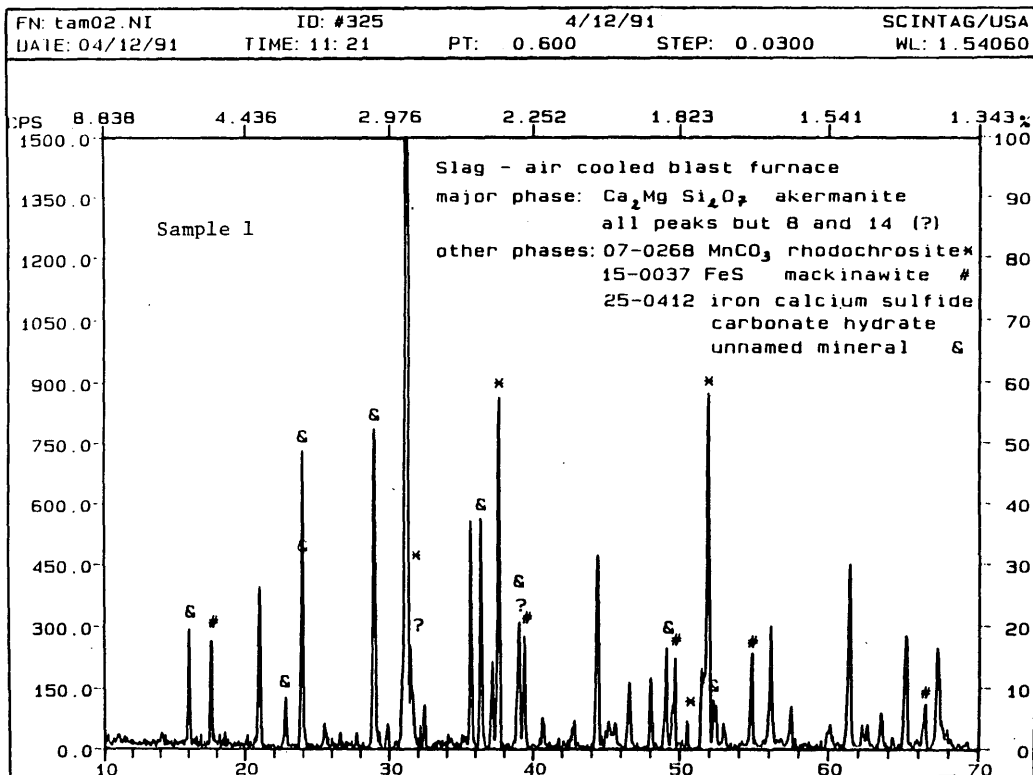


FIGURE 2 X-ray diffractogram of ACBF slag.

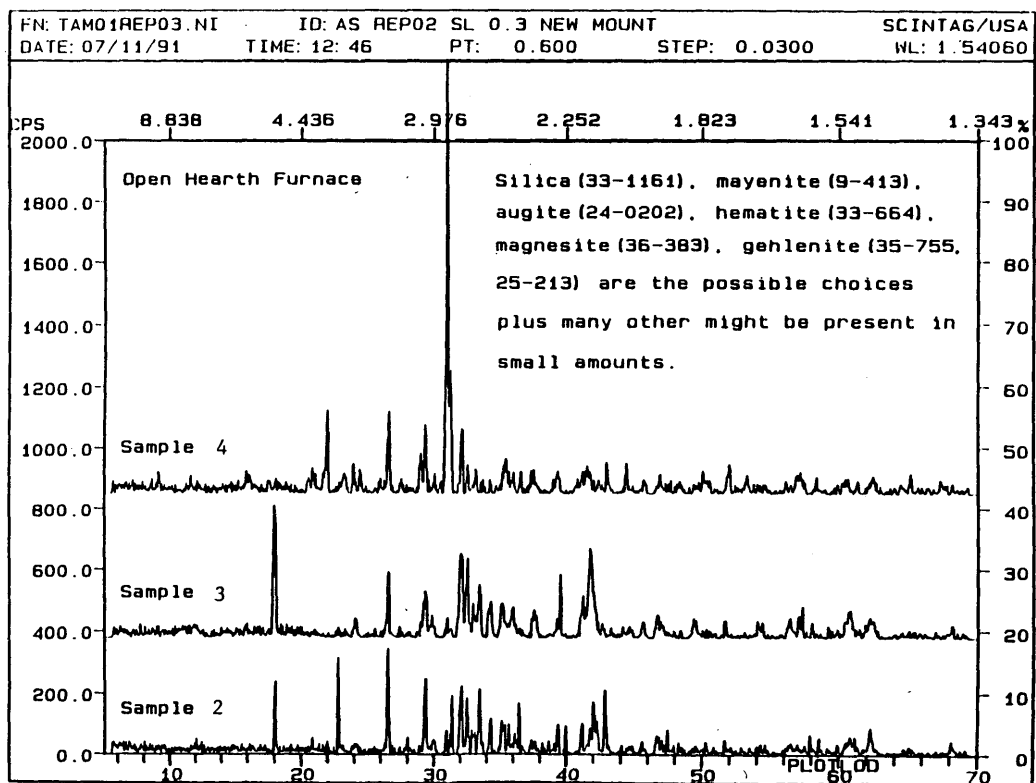


FIGURE 3 X-ray diffractograms of OH slag.

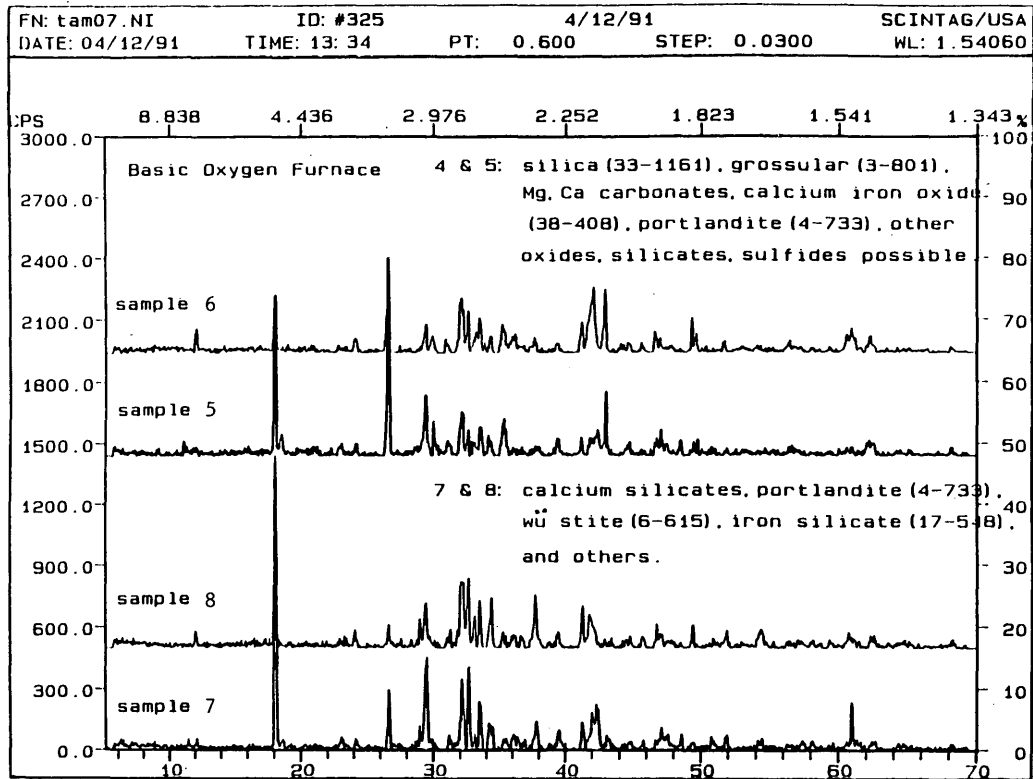


FIGURE 4 X-ray diffractograms of BOF slag.

### Leachate Analysis

In a leaching process, liquid passes through solids, where some of their contents are dissolved, and appears over the surface or outlet. When porewater passes through the slags containing free lime (CaO), a chemical reaction takes place forming calcium hydroxide and eventually calcium carbonate.

A special apparatus was designed for the leachate study. Thirty cylinders 12 in. high and 6 in. in diameter with an outlet facility at the bottom to draw water for analysis were made for this study. For each leachate experiment, 3000 g of deionized water was added

to 6000 g of slag in the cylinder. The pH and conductance of deionized water were recorded before adding it to the sample. The sample was kept undisturbed for 24 hr to permit the chemical reactions to occur. The pH of the leachate increased to more than 10.0 within 24 hr. Initially, the pH values increased approximately to 12 with time but after 10 days, pH values stabilized for all samples.

At the end of the fourteenth day, the leachate from each sample was collected in a beaker and filtered for the insoluble matter. The filtrate was kept in the oven until the water evaporated; no precipitate was recovered from the beaker. This result indicates that deionized water alone does not produce tufa from the slag.

TABLE 4 Surface Area Measurements for Slag Samples

Sample Number	Slag Type	Surface Area M <sup>2</sup> /Gm		
		BET/MP/SA <sup>a</sup>	BET/SP/SA <sup>b</sup>	LANGMUIR/SA <sup>c</sup>
1	ACBF	4.64	4.41	6.81
2	OH	3.05	2.84	4.54
3	OH	21.15	20.59	33.14
4	OH	14.61	23.84	22.78
5	BOF - Aged	11.20	10.88	17.69
6	BOF - Unaged	3.67	3.53	5.85
7	BOF - Aged	17.96	17.62	27.90
8	BOF - Unaged	11.44	11.00	16.63

<sup>a</sup> - BET/MP/SA - Brunauer, Emmett, and Teller Multi Point Surface Area

<sup>b</sup> - BET/SP/SA - Brunauer, Emmett, and Teller Single Point Surface Area

<sup>c</sup> - LANGMUIR/SA - Langmuir Multi Point Surface Area

Another set of experiments was conducted by passing carbon dioxide through the samples to accelerate tufa precipitation. The pH and conductance were recorded after the CO<sub>2</sub>-charged deionized water was added to the sample. Carbon dioxide at a rate of flow less than 0.2 ft<sup>3</sup>/hr was passed through the sample. The pH of the leachate was monitored constantly, and the carbon dioxide was passed until the pH of the leachate reached the pH of the deionized water. All the leachate water from the apparatus was drained out and collected in a beaker. After filtration, the filtrate was kept in the oven until the water evaporated; this time some residue was observed in the beaker. The residue was collected from the beaker for X-ray analysis. The diffractograms of the residue indicate that the composition was similar to tufa. This initial experiment was conducted for OH slag Sample 2 and BOF slag Sample 8 as a precursory effort to show that tufa is produced by CO<sub>2</sub>-charged waters.

X-ray diffraction analyses of all the leachate samples recorded as major phases the presence of calcite (CaCO<sub>3</sub>), aragonite (CaCO<sub>3</sub>), and halite (NaCl). In addition, one sample (OH-10) recorded the presence of bassanite, (CaSO<sub>4</sub> · 1/2 H<sub>2</sub>O) and two other samples (OH-3 and BOF-4) recorded the presence of magnesium carbonate hydroxide hydrate [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> · 4H<sub>2</sub>O].

#### Anhydrous Ethylene Glycol (Sugar Test)

Warm ethylene glycol (at 60°C to 70°C) has the property of dissolving only free lime (CaO). This property was used to determine the free lime present in the slag by titrating with 0.05 N HCl and with phenolphthalein as an indicator.

The results of the sugar test as percentages of free lime in the slag are as follows:

Sample	Aggregate	Percent Free Lime
1	ACBF slag	None
2	OH slag	0.237
3	OH slag	0.131
4	OH slag	0.044
5	BOF slag, aged	0.604
6	BOF slag, unaged	1.051
7	BOF slag, aged	0.691
8	BOF slag, unaged	10.64

Note that the ACBF slag possesses no free lime and therefore should not produce any tufa. The OH and BOF slags have some free lime content, and the unaged BOF slags possess more free lime than those that are aged.

A comparison of aged slag samples with the unaged slag samples indicates that the aging of slag has not helped sufficiently to reduce the free lime content because in the steel slags the residual free lime (CaO) is encapsulated by silicates. This encapsulation protects the CaO from hydration and the effect of CO<sub>2</sub>-charged porewater.

#### Variation of Free Lime Content with Stockpile Depth

ODOT requires slags to be aged for 6 months before they are used as subbase aggregates. Because stockpile aging does not necessarily remove all the free lime content of the slag, slag samples from different depths (0 to 7 ft at 1-ft intervals) in a stockpile were collected by a backhoe and analyzed for their free lime con-

tent by using the sugar test. The results of the analysis are as follows:

Depth (ft)	Percent Free Lime
0	0.096
1	0.185
2	0.265
3	0.335
4	0.388
5	0.401
6	0.451
7	0.579

The results indicate that the percent of free lime in the slag increases with an increase in the stockpile depth. Further analysis of the tufa produced in the laboratory from aged and unaged slag samples also confirms that aging does not totally eliminate the precipitation of tufa.

## FINDINGS AND CONCLUSIONS

### Findings

X-ray diffraction analyses determined that the slags are composed of complex aluminosilicates, ferrites, carbonates, and oxides of calcium, magnesium, and minor amounts of sulfides. The ACBF slag was found to be inert because no free lime (CaO) was found by the sugar test and the X-ray analysis did not show the presence of portlandite or calcite. Furthermore, this ACBF slag has a low SA and is primarily composed of crystalline calcium magnesium silicate (akermanite) as indicated by X-ray analysis.

The OH slags contain larnite ( $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>). The X-ray analysis also indicated the presence of calcite and portlandite. In addition, free lime was found in these samples by the sugar test. OH slag Samples 3 and 4 show more SA and should be more reactive than OH slag Sample 2, which has a lower SA; however, the high free lime content in OH slag Sample 2 gives it a high potential for tufa formation.

Both aged and unaged BOF slags contain free lime (CaO), portlandite [Ca(OH)<sub>2</sub>], and calcite (CaCO<sub>3</sub>). However, the aged samples have more CaCO<sub>3</sub> because of weathering and less free lime than the unaged samples. All OH and BOF samples produced tufa in the laboratory. High SAs in connection with the free lime, Ca(OH)<sub>2</sub>, and CaCO<sub>3</sub> content in all these samples should result in the formation of tufa.

The free lime content is not totally removed by stockpile aging and increases with stockpile depth as indicated by the sugar test. This is also confirmed through the tufa produced in the laboratory from aged and unaged slag samples. The amount of tufa precipitated by the slag aggregate depends on its original free lime content, SA, pore size distribution, effective porosity, and degree of weathering. The study indicates that OH and BOF slags will produce tufa, and only ACBF slag will not produce tufa.

### Conclusions

On the basis of the research study, the following conclusions are drawn for the continued use of slags as subbase aggregates in highway construction:

1. The ACBF slag can be used in highway construction,
2. The hydrophilic property of the aggregates may be responsible for water retention and precipitation of tufa,



3. Range of tufa precipitation varies with the SA,
4. Carbon dioxide is needed for the precipitation of tufa,
5. Stockpile aging of slag might reduce the rate of tufa precipitation but will not completely eliminate it, and
6. OH and BOF slags will produce tufa.

A further study on aging of OH and BOF slags should be conducted to document free lime content versus aging.

#### ACKNOWLEDGMENTS

This study was funded by the Ohio Department of Transportation (ODOT). The authors are grateful to the agency personnel, especially Bill Edwards, John Hurd; and Stu Schwotzer, for their constructive criticism. The authors also thank Jill Posta and Sridhar Katipally for typing this paper.

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*The opinions and viewpoints expressed are entirely those of the authors and not necessarily those of ODOT.*

*Publication of this paper sponsored by Committee on Subsurface Drainage.*