Determination of Original Free Lime Content of Weathered Iron and Steel Slags by Thermogravimetric Analysis

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Iron and steel slags are often used as subbase materials in the construction of highways. Previous studies have suggested that the free lime (CaO) in these subbases is responsible for the deposition of calcium carbonate (tufa) in many highway drains. Clogging of these drains leads to the deterioration of highways. Previous work has shown that if the total original CaO in slags exceeds 1 percent, the slags will readily produce tufa. Therefore, to classify the tufa-producing potential of these slags, it is necessary to determine the total original CaO. Thermogravimetry (TG) methods were employed and most of the TG plots indicated two major changes in weight loss—dehydroxylation of $Ca(OH)_2$ and dissociation of carbonates. From these changes in weight loss the percentage of CaO was calculated. These calculated percentages of CaO from the TG plot plus the results from the "sugar test" determine the total original percentage of CaO. Five groups are recognized according to the calculated total percentage of CaO: 0 percent, 3.5 to 5 percent, 8 to 9 percent, 10 to 12 percent, and 24 to 25 percent. Air-cooled blast furnace slag (0 percent CaO) is the only slag that should be used as a subbase in highway construction, whereas all others are considered to be harmful and could lead to the formation of tufa. TG methods and the sugar test are excellent and economical ways to characterize the original CaO in slags and the susceptibility of the slags to precipitate $CaCO_3$ in subdrains of highways.

Iron and steel slags from blast, open hearth, basic oxygen, and electric arc furnaces are often used as subbase materials in the construction of highways. Previous studies (1–3) suggest that the free lime (CaO) present in these subbase materials is responsible for the deposition of a chemical sedimentary rock composed of calcium carbonate called *tufa*. It is formed as a precipitate by the evaporation of water rich in dissolved calcium carbonate. This precipitate has been observed clogging many drains along highways in northeastern Ohio. Because the clogging of drains leads to highway deterioration, it is necessary to devise a rapid method to determine the total original CaO in these subbase materials.

PURPOSE AND SCOPE

The purpose of this study is to (a) characterize the slags, (b) determine the amount of "original" CaO in the weathered iron and steel slags, and (c) classify these slags according to their tufa-producing potential. The prepared samples were taken from stock-

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piles exposed to weathering for various lengths of time. Thermogravimetry (TG) analyses were performed on air-cooled blast furnace, basic oxygen furnace, open hearth, and electric arc furnace slags to determine the percent calcium hydroxide [$Ca(OH)_2$] and calcium carbonate ($CaCO_3$) in the samples. These percentages were added to the results from an extraction and titration method nicknamed the "sugar test" to determine the total original CaO—the free CaO content at the time the slag was in a molten state or just poured from the ladle. After determination of the total original CaO content, the slags were clustered and classified according to the total original percentage of CaO.

IRON AND STEEL SLAGS

Slag is produced during the manufacture of iron and steel. It is formed by the combination of oxidized impurities and flux. Flux is used to purge the ores of impurities, lower the melting point of the slag, and remove sulfur from the smelted iron. The types of slags that are produced vary greatly according to the extraction or refining processes used.

Blast Furnace Slag

Blast furnace slag is a by-product of the iron industry. The process begins when iron ore, a limestone flux, and coke are heated in a blast furnace. The iron ore is a mixture of oxides of iron, silica, and alumina. Preheated air is then blown into the furnace, and the oxygen combines with the carbon from the coke to produce heat and carbon monoxide. The carbon monoxide reacts with the oxides of the iron ore to produce iron. The silica and alumina of the iron ore combine with the calcium of the limestone to form the slag. Air-cooled blast furnace (ACBF) slag is one that is allowed to solidify under normal atmospheric conditions. Water is sometimes sprayed on the slag to accelerate cooling and to induce cracks. Table 1 records the range of compositions for blast furnace slags.

Steel Furnace Slags

In the steel-producing industry three types of furnaces are used: open hearth, basic oxygen, and electric arc. The actual heating and smelting methods are very similar for each type of furnace;

TABLE 1   Range of Composition for Blast Furnace Slags (4)

Compound	Range Percent	Typical Analysis
SiO_2	33–42	36.4
Al_2O_3	10–16	12.8
CaO	36–45	41–43
MgO	3–12	5.8
FeO	0.3–2.0	0.4
Fe_2O_3	–	0.5
FeO + Fe_2O_3	0.2–1.5	1.4
MnO	–	1.3
S	1.3	–
P_3O_5	–	–

Modified from T. Segal [4]

however, there are some minor differences between the steel furnaces. In open hearth (OH) furnaces the limestone is added along with the scrap steel. The OH furnace takes about 5 to 14 hr to produce 300 tons of steel, whereas it would take the basic oxygen furnace (BOF) only 45 min to produce an equivalent amount. In the BOF, oxygen is blown onto the top of the charge at supersonic speed before the flux is added. Another steel furnace is the electric arc furnace (EAF) in which graphite electrodes are used for the heating process. Table 2 gives a range of compositions for OH, BOF, and EAF slags.

CHEMISTRY AND MINERALOGY OF SLAG SAMPLES

The chemical analyses of the slag samples used in this study are shown in Table 3. The process involved heating the slag in a crucible over an open flame until dehydration was complete. The samples were analyzed for elemental and oxide content by X-ray fluorescence (XRF) methods. These analyses were normalized to include the hydroxyl water and CO_2 data gleaned from the TG studies.

X-ray powder diffraction analysis was used to determine the gross mineralogy of the slags (5). Search-and-match routines were used against the ICPDS data base for the identification of the

resulting peaks. Many minerals typical of these slags were identified, but for brevity they are not listed here. Of importance to this study, however, is the identification of $Ca(OH)_2$ and $CaCO_3$ in all the slags except the ACBF sample (No. 1). These chemical species should not be present in an unweathered slag. They would have been dissociated to CaO because of the high temperature of the original molten slag. The presence of $Ca(OH)_2$ and $CaCO_3$ in the stockpiled slags is assumed to be due to weathering. Residual CaO is present because some of it is encapsulated by silicates. This encapsulation protects the CaO from the effect of CO_2-charged porewater.

THERMAL ANALYSIS

Thermal analysis is the study of chemical and physical changes in a given material due to changes in temperature. These temperature changes are usually linear with time. The changes in enthalpy that accompany chemical and physical changes can be observed and recorded. These enthalpic changes, either exothermic (+) or endothermic (−), are caused by phase transitions such as fusion, crystalline structural inversions, boiling, sublimation, and vaporization; dehydration reactions; dissociation or decomposition reactions; oxidation and reduction reactions; destruction of crystalline structures; and other chemical reactions. Generally, phase

TABLE 2   Range of Composition for Steel Furnace Slags*

Compound	Open Hearth		BOF**	EAF**
	Range %	Typical Analysis %	Range %	Typical Analysis %
SiO_2	16–19	18.4	7.2–18.2	13.9
Al_2O_3	2–3	2.5	0.42–3.0	2.8
CaO	40–55	45.0	36–49	48.3
MgO	5–7	5.9	5–12	9.9
FeO	–	12.2	15–30	15.0
Fe_2O_3	–	3.4	N/A	N/A
FeO + Fe_2O_3	10–23	15.6	N/A	N/A
MnO	5–6	8.6	N/A	N/A
S	0–1	–	0.05–0.5	0.06
P_2O_5	–	–	0.03–0.9	0.88

* Modified from T. Segal [4] and synthesized from 50 analyses furnished by J.M. Olle, Edward C. Levy Co. 8800 Dix Ave., Detroit, MI 48209
** From Olle, J.M., 1991, Personal correspondence

transitions, dehydration, reduction and some decomposition reactions produce endothermic effects, whereas crystallization, oxidation, and some decompositions produce exothermic effects. Researchers (6–10) since the mid-century have made important contributions to thermal analysis.

There are five basic categories or techniques of thermal analysis: thermometry, differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis and dilatometry (TMA), and thermogravimetry (TG). The last technique was used in this study.

THERMOGRAVIMETRY

TG analysis measures the loss or gain of weight by a substance as its temperature is raised or lowered at a constant rate. The reactions that occur during the heating process are responsible for the changes in weight. Knowing that certain reactions occur at specific temperatures enables the identification of the constituents of the sample. The data from the experiment are then recorded as a TG plot of mass versus temperature or time. From the TG plots, the composition of a sample can be determined. The physicochemical applications of thermogravimetry are given in Table 4 (10). Also from the TG plot, the first derivative can be calculated with respect to either time or temperature; this is called derivative thermogravimetry (DTG). The calculations can be done either by the TG thermal balance or by a computer program. The derivative is usually superimposed on the TG plot (see Figure 1). The DTG plot is set up so that temperature or time is on the abscissa, increasing from left to right, and the derivative values are on the ordinate, increasing from bottom to top. The DTG plot is used to help locate the start, peak, and end temperatures of a given reaction.

METHOD OF ANALYSIS

A high-temperature (1400°C) thermobalance was used to measure weight gain or loss during heating. The sample and operational parameters employed in this study are weight, 9 to 10 mg; grain size, +325 mesh; atmosphere-nitrogen flow rate, 30 ml/min; heating rate, 20°C/min; and water flow rate, 300 ml/min. The instrument was calibrated using melting and magnetic standards. In addition, a further check for accuracy was made by using a calcium oxalate ($CaC_2O_4 \cdot H_2O$) standard. These calibrations were repeated every 25 runs.

DISCUSSION AND RESULTS

Analysis of TG Plots

Most of the TG curves indicate two major changes in weight loss. This doublet is evidence of a two-stage reaction that is characteristic of OH, BOF, and EAF steel slags. All samples were preheated to 350°C to drive off any chemiabsorbed water. The first-stage reaction is caused by the evolution of hydroxyl water at about 400°C and ending at about 460°C. The second stage of decomposition is the evolution of carbon dioxide from the calcium carbonate in the slag, which occurs at about 490°C and ends at about 785°C. These reactions are detailed below:

$$Ca(OH)_2 + heat \rightarrow CaO + H_2O \uparrow$$

$$CaCO_3 + heat \rightarrow CaO + CO_2 \uparrow$$
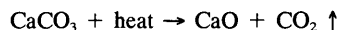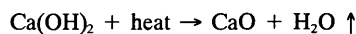
The first derivative of the TG curve, DTG, was superimposed on each of the plots, excluding the ACBF sample (No. 1), for which no reactions occurred throughout the heat. In this study DTG was used to indicate the initial peak and final temperatures of the reaction of the TG plots.

The first reaction, if present, is labeled 1 at the point at which the reaction begins and 2 at the point at which the reaction ends. These numbers were determined, as mentioned before, from the first derivative. The temperature and percent weight loss for these numbers are found in the box labeled POINT TABLE on the left side of each plot. The value that is located between the numbers 1 and 2 on the curve is the extrapolated onset temperature, which is determined from the computer program.

The initial and final temperatures and the percent weight loss of the second reaction, if present, are labeled by the two-point angle. Again, these points were determined from the DTG plot.

TABLE 3   Oxide Analysis of Slags

Sample No.	Sample Type	Al_2O_3	CaO	Fe_2O_3	MgO	Mn_2O_3	P_2O_5	K_2O	SiO_2	Na_2O	SO_3	$(H_2O)_{os}$	CO_2	Others
1	ACBF	8.52	40.09	0.85	10.80	0.71	<0.02	0.24	38.09	0.23	0.24	0.04	–	0.18
2	OH	3.50	36.02	26.57	9.84	3.31	0.26	0.01	15.19	0.06	1.70	0.42	3.13	– 1.13
3	OH	3.57	40.76	23.81	7.81	5.26	0.10	<0.01	13.73	<0.01	<0.01	0.78	1.51	
4	OH	4.66	34.02	15.41	5.04	3.39	0.10	0.17	26.06	0.08	<0.01	0.57	10.49	1.79
5	BOF	3.75	35.27	24.08	10.52	2.81	0.29	<0.01	12.77	0.08	<0.01	3.08	5.54	2.54
6	BOF	4.46	38.49	26.33	8.35	4.48	0.13	<0.01	12.41	0.07	0.01	0.61	2.11	–
7	BOF	2.97	48.02	15.05	9.67	3.12	0.22	<0.01	13.21	0.01	<0.01	2.65	6.06	–
8	BOF	3.01	50.81	15.62	5.32	3.56	0.30	<0.01	15.04	<0.01	0.04	2.88	3.40	
9	EAF				Oxides Not Determined								2.36	17.02

Others, commonly include: SrO, BaO, TiO_2, Cr_2O_3, and V_2O_5
Dash (–) indicates not detected.

TABLE 4   Applications of Thermogravimetry

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Physical Changes

        Sublimation
        Vaporization
        Absorption
        Adsorption
        Magnetic properties
          Curie temperature
          Magnetic susceptibility

    Chemical changes

        Solid → gas

          Thermal decomposition of many organic and polymeric substances
          Pyrolysis of coal, petroleum, and wood
          Thermal oxidation degradation of polymeric materials
          Carbon gasification with oxygen, steam, or carbon monoxide
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$Solid_1 \rightarrow solid_2 + gas$
        or
$Solid_1 + solid_2 \rightarrow solid_3 + gas$

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          Thermal decomposition of many inorganic materials
          Roasting and calcining of minerals
          Determination of moisture, volatiles, and ash contents
          Dehydration studies
          Dehydroxylation studies
          Decomposition of explosives
          Development of analytical procedures
          Kinetic studies (also applicable to solid - gas)
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$Solid_1 + gas \rightarrow solid_2$

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SAMPLE  :  SLAG
RUN ID  :  # 3                    GASES   :  NITROGEN
SIZE    :  10.008 mg              SOURCE  :  O.H.
```
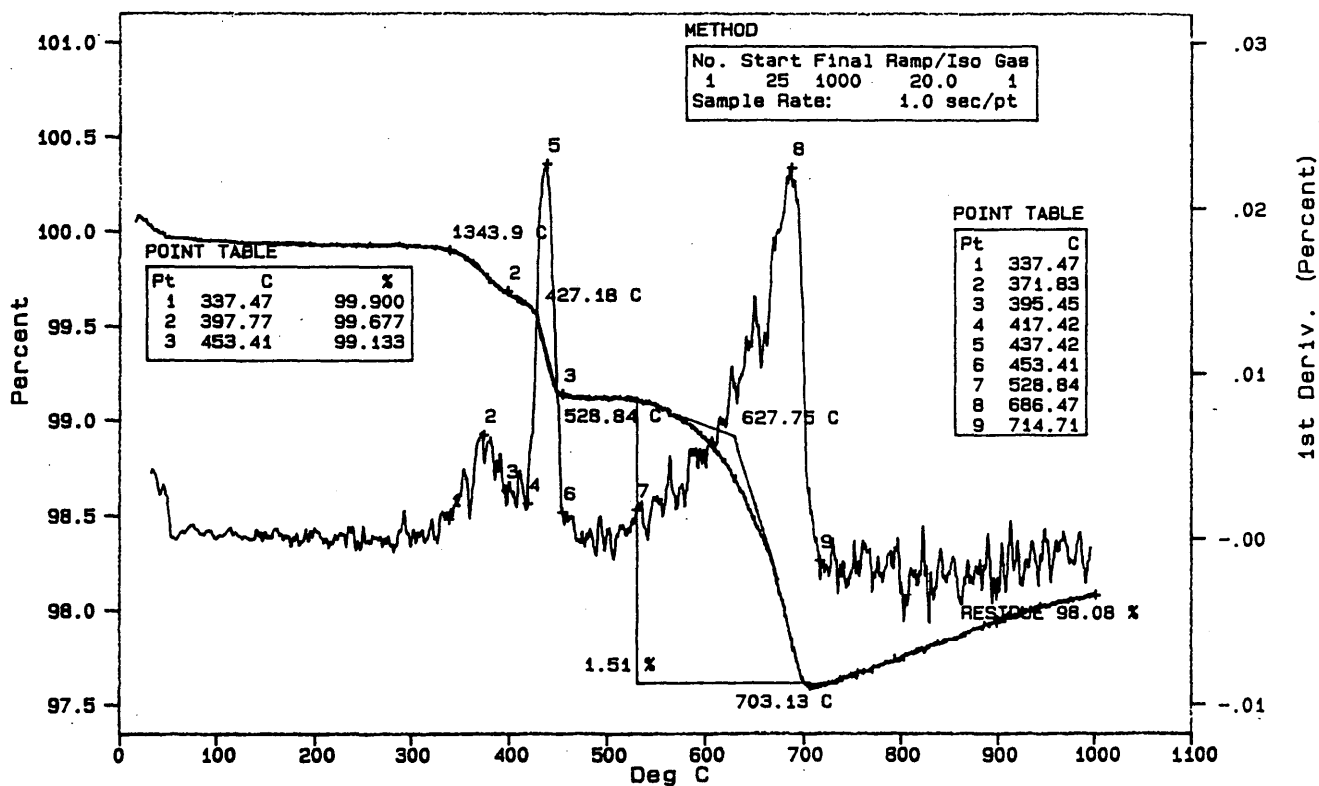

FIGURE 1   TG plot of sample No. 3, OH slag.

TABLE 5   Data from Thermogravimetric Analysis

Sample #	Dehydroxylation of Ca(OH)₂ I.T.[1]	O.T.[2]	P.T.[3]	F.T.[4]	%(OH)₂ Loss	Dissociation of CaCO₃ I.T.[1]	O.T.[2]	P.T.[3]	F.T.[4]	% CO₂ Loss
1 (ACBF)	No reaction occurred					No reaction occurred				
2 (OH)	416.07	430.85	441.95	459.95	0.20	517.40	668.81	709.92	731.37	3.18
3 (OH)	397.77	427.18	437.42	453.41	0.54	528.84	627.75	689.90	703.13	1.51
4 (OH)	Reaction not measurable					674.04	712.14	743.49	766.87	6.65
5 (BOF)	408.78	441.81	448.79	464.19	0.96	509.22	658.51	708.55	734.15	5.55
6 (BOF)	402.60	418.77	430.92	453.94	0.32	549.26	648.32	686.73	705.63	2.11
7 (BOF)	404.61	435.13	446.45	462.17	0.89	487.57	655.16	709.81	737.46	6.16
8 (BOF)	408.80	430.54	443.24	460.02	0.87	543.39	660.14	703.21	723.79	3.52
9 (EAF)	424.31	448.49	452.52	466.12	0.75	561.76	708.74	763.82	783.03	17.20

*1 Initial temperature.   2 Onset temperature.   3 Peak temperature.   4 Final temperature.*

These temperatures and percentages were determined from the TG and DTG curves.

The extrapolated onset temperature is located to the right of the reaction. The plot for sample No. 3 is shown in Figure 1 and illustrates the double reaction, point table, and the first derivative. The TG curve in Figure 1 is labeled as mentioned above, with the residue located at the end of the curve. The peak temperatures for the two reactions are labeled on the derivative. All values for the reactions that occurred in the samples are given in Table 5, which also records the percent weight loss for (OH)₂ and CO₂ for the nine slag samples.

Method Used To Determine Total Original Percentage CaO

The total original percentage of CaO is calculated by addition of the results from the sugar test, calculated percentage of CaO due to dehydroxylation of Ca(OH)₂ (first reaction), and the calculated percentage of CaO due to dissociation of CaCO₃ (second reaction).

The sugar test (11) determined the CaO in the slag aggregates by dissolution and extraction of the CaO by hot (60 to 70°C) anhydrous ethylene glycol. The CaO is determined by titration with 0.05 N HCl and phenolphthalein as the indicator (see Table 6). The CaO percentages are calculated by using the values for sample No. 3 from Table 5, such as percent hydroxyl water loss, 0.54; percent CO_2 loss, 1.51; and by using the mole weights from the reaction. As stated previously, the reactions that occur are

$$Ca(OH)_2 + heat \rightarrow CaO + H_2O \uparrow$$

$$CaCO_3 + heat \rightarrow CaO + CO_2 \uparrow$$
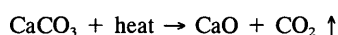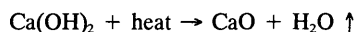
The mole weights for each of the components are as follows:

$CaO = 56.079 = 56; H_2O = 17.99 = 18; Ca(OH)_2 = 74.096 = 74;$

$CaCO_3 = 100.088 = 100;$ and $CO_2 = 44.079 = 44.$

TABLE 6   Total Original Percentage of CaO by TGA

Sample #	% CaO[*]	% CaO₍OH₎₂[**]	% CaO₍CO₃₎[***]	Total % CaO	Rank/ Cluster
1 (ACBF)	0	N/D	N/D	0	1
2 (OH)	0.237	0.622	4.047	4.906	2
3 (OH)	0.131	1.692	1.922	3.745	2
4 (OH)	0.044	N/D	8.464	8.508	3
5 (BOF)	0.604	2.971	7.064	10.639	4
6 (BOF)	1.051	0.992	2.685	4.728	2
7 (BOF)	0.691	2.775	7.840	11.306	4
8 (BOF)	1.064	2.700	4.480	8.244	3
9 (EAF)	0.602	2.340	21.891	24.833	5

N/D = Not Determinable
*   * Data derived from anhydrous ethylene glycol, 'sugar test'*
* ** Calculation of % CaO due to dehydroxylation of Portlandite (Ca(OH)₂)*
* *** Calculation of % CaO due to dissociation of carbonates*

The equations are set up as follows to calculate the percentage of CaO:

$$\frac{CaO}{56} = \frac{H_2O \text{ delta wt. loss}}{18} \quad (1)$$

$$\frac{CaO}{56} = \frac{CO_2 \text{ delta wt. loss}}{44} \quad (2)$$

Now the percentage of CaO is easily calculated, that is, using the values 0.54 and 1.51 (from Table 5 for sample No. 3) and cross-multiplying, as shown below:

$$\frac{CaO}{56} = \frac{0.54}{18} = 1.692 \text{ percent CaO} \quad (3)$$

$$\frac{CaO}{56} = \frac{1.51}{44} = 1.922 \text{ percent CaO} \quad (4)$$

The final step in determining the total original percentage of CaO is to add the three percentages of CaO together as shown in Table 6.

From the studies by Narita et al. (*12*), weathering slag is related to the amount, distribution, and characteristics of the CaO. If the unweathered slag contains less than 1 percent CaO, it should be volumetrically stable and should not produce tufa. If, however, the original amount of CaO is in excess of 1 percent, the slag should readily produce tufa in subdrains of highways. All slag samples are grouped in Table 6 according to their range of total original percent CaO. Five groups are recognized: 0 percent, 3.5 to 5 percent, 8 to 9 percent, 10 to 12 percent, and 24 to 25 percent. ACBF slag (0 percent CaO) is the only one that can be used as a subbase in highway construction; all others are considered to be harmful and could lead to the formation of tufa.

CONCLUSIONS

Previous work (*12*) has shown that if the percentage of total original CaO in a slag exceeds 1 percent, the slag could readily precipitate $CaCO_3$. The results from the TG plots showed two major changes in weight loss—dehydroxylation and dissociation of carbonates. From these changes in weight loss, the percentage of CaO can be calculated. These calculated percentages of CaO from plots plus the results from the sugar test determine the maximum *original* percentage of CaO. ACBF slag (0 percent CaO) is the only one that can be used as a subbase in highway construction; all others are considered to be potentially deleterious and could lead to pavement failure. The TG method together with the sugar test

are excellent and economical ways to determine the maximum original CaO in slags and the tendency of the slags to precipitate $CaCO_3$ in the subdrains of highways.

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