Favorable slag composition is essential to maximize on-line time of the slagging incinerator.

by Paul B. Queneau, Douglas E. Cregar, and Leonard J. Karwski

DuPont operates 21 waste incinerators for liquids and/or solids at 12 of its U.S. plants. The company’s first rotary-kiln incinerator was brought on line 17 years ago at Laplace, La. The kiln was designed to generate ash rather than slag. Modifications have since been made on its ash-handling system to minimize operating problems caused by inadvertent formation of slag.

A second, much larger rotary-kiln incinerator became operational in 1990 at DuPont’s Sabine River Works in Orange, Texas. The kiln, manufactured by Deutshe Babcock, can operate efficiently in either slagging or ashing mode. It is currently run as an ashing processor; processing a wide variety of wastes generated at six DuPont plants located along the Gulf Coast.

A rotary-kiln incinerator is a refractory-lined cylindrical tube mounted at an incline from the horizontal plane. This tube is rotated to facilitate mixing of the wastes under incineration with combustion air that can be enriched with oxygen. Incineration kilns normally operate with cocurrent flow, i.e., solids and gas flow in the same direction.

The dust-laden combustion gases flow into a second combustion chamber, or afterburner. The afterburner is a refractory-lined vertical or horizontal chamber into which additional clean fuel and/or liquid waste and air are introduced to complete combustion (Figure 1).

Ashing vs slagging kilns

Kilns can operate over a broad range of temperatures, allowing solid residuals to exit as either ash or slag. The slope, or rake, of a kiln operated in the slagging mode can be adjusted to maintain a pool of molten slag at the discharge lip. In the ashing mode, kiln rake is normally 2 to 4 percent, with the higher end at the feed end of the kiln. Ashing incinerators have a propensity to form unwanted slag, not only in the furnace but also in exhaust ducts and in the afterburner compartment.

Even when a kiln is adjusted for the higher temperature slagging operation (1100° to 1300°C), the slag causes operating problems. It can become too viscous or thick, forming rings that plug the kiln and disrupt slag granulation. It can become too thin, exposing and eroding refractory, or reducing hold-up time. It can fail the Environmental Protection Agency’s Toxicity Characteristic Leachate Procedure (TCLP) for characteristic or listed wastes, requiring either recycle or stabilization prior to landfill.

An ideal condition would be the controlled generation of slags that are consistently
Figure 1. Cross-section of DuPont's Sabine River Works rotary-kiln incinerator, which can operate in either an ashing or a slugging mode.
Furnace slag control has now become more of a science than an art.

- Combustion gases from a rotary-kiln incinerator flow into a second combustion chamber, or afterburner. Fuel and air are introduced to complete combustion.

the proper viscosity, don't corrode the refractory liner, and are sufficiently stable for use as fill and construction materials — instead of requiring storage in a landfill.

Incineration vs smelting

Metallurgists have for centuries encountered problems similar to those of incinerator operators. Roasters designed for ashing start slagging; smelters designed for slagging build up solid accretions. The principles applied for smelter slag formulation also are used by the roaster engineer to avoid slagging. It is therefore appropriate to transfer slag technology from metallurgical practice to the incineration industry.

Incinerator slags tend to be formulated more as a result of whatever is in the feed, rather than as the result of close coordination between feed acquisition groups and incinerator process engineers. A difficulty is that there are multiple constraints on incinerator feed composition. Constraints include safety and government regulations, feedstock availability and pricing, energy content and physical form. There are also emission limitations on certain components such as halides and metals. As a result, the kiln operator seldom knows the composition of the slag in the kiln and, therefore, relies on experience and intuition to maintain throughput.

On the other hand, metallurgical slags tend to be carefully managed, since feedstocks are usually from familiar sources. Centuries of operating experience have proved that slag quality is critical to economic viability. Slag management is thus greatly facilitated. Understanding methods developed by pyrometallurgists for formulating slags friendly to both the furnace and the environment may result in better operation of waste kilns and better quality of waste-derived slags.

Slag morphology

The question has been asked: Why would one want to make a slag? Slag brings to some the image of solids that are inherently polluting. In fact, several Superfund sites are the direct result of slags releasing heavy metals — especially lead, cadmium and arsenic. However, a slag need not be unstable. Therefore, before discussing the ways to control slag formation, let us examine why it is reasonable to form a slag.

Slag is a fused inorganic residue from high-temperature furnace operations. It is made up primarily of common inorganic oxides, the most essential of which is silica. Slag contains no organics; it should be relatively uniform in composition. Clinker

Liquid Range of FeO-A1₂O₃-SiO₂ Slag at 1200°C

- Figure 2. Slag melting point can be estimated using ternary phase diagrams.
and ash generated from low-temperature incinerator operations are not slags. Wastes that generate environmentally hazardous ash can produce environmentally stable slag when incinerated in a slagging mode. Note that operating in the slagging mode substantially increases kiln operating costs. Rotary-kiln incinerators capable of slagging operation also incur higher capital cost.

We can look to nature for examples of stable slags. Igneous rock is a slag generated from magma, tested for environmental stability over geologic time. Study of weathering processes has developed considerable amounts of data for predicting the effect of the environment on various rocks and minerals.

Igneous rock, such as basalt, and slag are silicates. Silicates make up about 93 percent of the earth's crust. They consist of SiO₄ tetrahedrons that incorporate heavy-metal atoms. Environmental stability of silicate rock or slag depends on the strength of its silicate network. Silica and other acidic oxides, such as alumina (Al₂O₃) and ferric oxide (Fe₂O₃), are network chain formers. Basic oxides, such as sodium oxide (Na₂O) and lime (CaO), are chain breakers; so are sulfide and chloride. The higher a slag's content in acidic oxides, the more weather-resistant the structure tends to be.

How much of a given heavy metal can be incorporated in a silicate slag will depend on that metal's similarity to other atoms already present. The likelihood of a given substitution can be estimated by comparison of "replacement indices" calculated from the ion's radius, charge, coordination number and electronic configuration. Referring to Table 1, one would predict that slag high in calcium (Ca²⁺) content could be a good host for cadmium (Cd²⁺) and lead (Pb²⁺).

Rapidly cooling a slag makes it easier for heavy metals to "find a home" within the slag. This process is called vitrification; one method of vitrifying is granulation in water. The more rapid a slag's cooling rate, the more irregular the silicate network of the solidified slag. The greater the network irregularity, the greater the opportunity for heavy metal ions not compatible with the ordered structure to become incorporated.

Slags in commerce

Safe use of slags derived from wastes provides further evidence that slags can in fact be environmentally safe. Examples in the United States include slag from processing electric arc furnace (EAF) dust, chromium plating sludges and spent nickel-cadmium batteries. Slag generated in West Germany during incineration of non-hazardous waste must by law be recycled so far as is technically feasible and economically justified. In Japan, municipalities have constructed facilities to vitrify ash, sewage sludge and industrial waste; slag output is used in construction applications.

Markets for slag, be it derived from smelting or waste incineration, include aggregate for concrete, pavement block, pipe bedding, frost-protection layer, noise protection walls, sea walls, mineral wool insulation, roofing, sand-blasting grit and fill.

U.S. consumption of slag in 1989 was approximately 21 million tons, 95 percent of which was derived from iron and steel production.

Slag optimization

There are two goals in optimizing slag properties. The first is to promote efficient furnace operation. The second goal is to form an environmentally stable slag. For practical purposes, in U.S. waste incinerators, this translates to passing the TCLP test so the slag can be landfilled without further stabilization. Factors conclusive to slag environmental stability — composition and rate of solidification — have already been addressed. The remainder of this presentation therefore focuses on slag optimization for efficient incinerator operation.

The four primary slag control parameters are fusion temperature, molar basicity, apparent viscosity and oxidation state. To the extent market and regulations allow, the operator uses feedstock mixes that minimize flux addition. Flux calculations are computerized.

The waste incinerator industry has limited opportunity to blend consistent uniform feedstocks. However, efforts in this direction are increasing, with such practices as providing discounts to encourage large-volume, well-mixed waste deliveries and increasing storage capacity to blend larger waste volumes.

Slag fusion temperature

A given mixture of combusted incinerator solids melts over a range of temperatures. The first liquid typically appears at the "eutectic" temperature; melting is complete at the "liquidus" temperature. Larger sized or more refractory materials with high melting points (such as shredded drums) may remain unmelted. For on-line control of slag fusion temperature, one needs either a measurement of slag liquidus temperature or an analysis of the slag. An incineration operator can have access to both on a timely and economic basis.

Slag liquidus temperature, as well as its melting range, is obtained via the ASTM D1857-87 ash fusion procedure. This test is routine in the coal industry. After removal of metallics and unfused oxides, the sample is ground and molded into a cone. The cone is heated in a controlled atmosphere and its melting range recorded.

On-line control of slag assay is further enhanced by installing an X-ray fluorescence (XRF) system for slag analysis. Data accumulated in a microproces-
Slag molar basicity

Molar basicity calculations help to identify slags that have acceptable liquidus temperature, viscosity and refractory compatibility.

Calculation of molar basicity is straightforward. Divide the sum of the slag's basic oxides by the sum of its acidic oxides, on a mole percent basis. For example, a slag containing 55 percent FeO (basic) and 45 percent SiO₂ (acidic) has a molar basicity of 1.0, i.e., (25/72) divided by (45/60), where 72 and 60 are the atomic weights of the two oxides. This slag is neutral, i.e., neither basic nor acidic.

Acidic oxides readily incorporate into a silicate polymer network. Besides silica, the common acidic oxides are P₂O₅, Al₂O₃, Cr₂O₃, TiO₂, and ZrO₂; note that each has a valence greater than or equal to 3. Basic oxides are those that break, rather than extend, the slag's silicate network. Monovalent and divalent oxides, such as Na₂O and CaO, respectively, are basic. In silicate slags, sulfide and chloride are also basic, which surprises those who are familiar with their strongly acidic nature in aqueous systems.

When calculating slag basicity, iron can be a special problem. Ferrous oxide (FeO) is a reasonably strong base. However, ferric oxide (Fe₂O₃) is a weak acid. For slags containing Fe₂O₃, it is suggested that half of the ferrous iron be treated as acidic, the other half as basic. Treat all of the FeO as a base.

Now let us make use of the molar basicity concept. You are monitoring the basicity of your incinerator slag; the kiln is running well. However, slag basicity is generally decreasing due to the waste's decreasing clay content. The following rules of thumb apply: Increasing basicity tends to increase slag liquidus temperature but decrease liquid-phase viscosity (to be discussed). The more basic the slag, the more basic the refractory used to contain it.

If slag molar basicity is between 0.9 and 1.3, slag fluidity (the reciprocal of viscosity) is likely to be acceptable — if the slag has been heated to above its liquidus temperature. This additional constraint on slag composition is illustrated by the green region of the right-hand ternary in Figure 2.

Slag viscosity

A slag having acceptable liquidus temperature (less than 1300°C) and molar basicity (approximately 0.9 to 1.3) is likely to be reasonably fluid. Viscosity is dictated more by slag composition than by temperature. For incineration, a target apparent viscosity is about 25 poise, i.e., that of a SAE 70-wt lubrication oil. The higher the viscosity, the less fluid the slag. In rotary-kiln incinerator operation, apparent viscosities less than 10 poise should be avoided; excess fluidity accelerates refractory brick erosion and slag penetration. An apparent viscosity greater than 200 poise leads to slag buildup within the kiln. On-line determination of incinerator slag flowability has reportedly been achieved in Japan by correlating this property to the luminance of the slag.

One targets for a viscosity low enough to permit slag mixing and discharge from the furnace, yet high.

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**Table 1**

<table>
<thead>
<tr>
<th>Ionic Replacement</th>
<th>Indices Of</th>
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<tbody>
<tr>
<td>Na⁺ = 0.06</td>
<td>Ni²⁺ = 0.14</td>
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<tr>
<td>Ba⁺² = 0.07</td>
<td>Cu⁺⁺ = 0.14</td>
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<tr>
<td>P⁺³ = 0.08</td>
<td>Mg⁺² = 0.14</td>
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<tr>
<td>Ca⁺⁺ = 0.09</td>
<td>Cr⁺⁺ = 0.22</td>
</tr>
<tr>
<td>Cd⁺⁺ = 0.09</td>
<td>Fe⁺⁺ = 0.22</td>
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<tr>
<td>Zn⁺⁺ = 0.14</td>
<td>Al⁺⁺ = 0.35</td>
</tr>
<tr>
<td>Fe⁺⁺ = 0.14</td>
<td>Si⁺⁺ = 0.48</td>
</tr>
<tr>
<td>Cu⁺⁺ = 0.14</td>
<td>As⁺⁺ = 0.60</td>
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**Table 2**

<table>
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<tr>
<th>Effect Of Solids On Slag Viscosity</th>
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<tr>
<td><strong>Solids, Volume %</strong></td>
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<tr>
<td>0</td>
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<td>10</td>
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Figure 3: The interrelationships between temperature, basicity and viscosity parameters are illustrated.
Forewarned is forearmed when it comes to avoiding slag-ring buildup on the refractory.

enough to maintain a protective boundary layer on furnace walls. Silicate chain-formers, i.e., the acidic oxides, decrease slag fluidity. Basic oxides, the chain breakers, increase fluidity if the slag remains molten. Caution: adding excess base can lead to solids precipitation.

Recall the rule of thumb: Increasing basicity tends to increase slag liquidus temperature.

Fine solids suspended in the slag increase slag viscosity. Table 2 illustrates the suspended solids effect to solids precipitation. The term “apparent viscosity” includes both the viscosity of the solids-free liquid and the additional viscosity imparted by suspended solids.

Above 35 percent solids the slag can become pseudoplastic, i.e., apparent viscosity decreases as shear increases. “Shear-thinning” is one reason rotary furnaces are so effective in processing feedstocks that are difficult to flux.

It turns out that absolute viscosity can be calculated with surprising accuracy. Inputs are slag analysis and temperature. A computer-equipped kiln operator can thus keep track of slag viscosity trends. This capability can be of substantial value. Forewarned is forearmed when it comes to avoidance of slag-ring buildup on the refractory.

Two more rules of thumb are as follows. When slag silica content exceeds 45 percent, slag fluidity usually suffers; high-silica slags are especially viscous if alumina is also high (greater than 10 percent Al₂O₃). Magnesia (greater than 8 percent MgO) and chrome (greater than 4 percent Cr₂O₃) tend to react with Al₂O₃ and FeO to form insoluble spinel-type precipitates; unacceptably high viscosity can result.

Figure 3 shows graphically the interrelationships between temperature, basicity and viscosity parameters. In this case the ternary diagrams include two chain breakers (FeO and CaO) and two chain formers (SiO₂ and Al₂O₃). Blue lines trace the eutectic compositions; the two ternary eutectics (1070°C and 1110°C) are circled. These are the minimum-melting-point compositions. The minimums occur at intermediate levels of silica (34 to 43 percent SiO₂) and alumina (10 percent Al₂O₃). Also consistent with the “rules of thumb” is the lower melting point of the more acidic ternary eutectic.

As expected, the eutectic closer to the acidic SiO₂ corner has a lower basicity, i.e., 0.77 vs 1.2. The bottom two diagrams in Figure 3 give the approximate temperatures (Tₙₐ₀) to which the two ternary eutectic melts must be heated to attain about 20 poise viscosity. The more acidic eutectic requires higher temperature to achieve comparable viscosity. Addition of 5 percent NaCl, a strong slag fluidizer, decreases the Tₙₐ₀ values by more than 100°C.

**Slag oxidation potential**

A slag can be oxidizing or reducing, depending on its Fe²⁺/Fe³⁺ ratio. Slag oxidation potential in a rotary kiln is surprisingly independent from that of combustion gases with which it interfaces. Slag remains reducing until residual carbon, metallics and other reductants are burnt out. Slag oxygen potential is usually measured via a disposable-tip EMF electrode.

The effect of slag Fe²⁺/Fe³⁺ ratio, a measure of oxygen potential, on slag properties should not be underestimated. Excessive slag reduction can result in unwanted formation of metallics, which can cause pressure surges during slag granulation. As a slag oxidizes, its liquidus temperature tends to increase. The mixed oxide, magnetite (Fe₃O₄), has a low solubility in silicates low in CaO content; it precipitates as a fine solid suspension that increases slag viscosity.

**Conclusion**

Slag properties, including environmental stability, can be predicted and managed. Hazardous waste incineration in a rotary kiln is a process that is not inherently conducive to forming uniform, stable slags. However, understanding the technology involved can significantly improve furnace operation and potentially generate environmentally stable slags that could in some cases have commercial value.

Paul Queneau is a project manager for Hazen Research, Golden, Colo. Douglas Cregar is a senior engineer associate and Leonard Karwaski is a research associate, both with E.I. du Pont, Chambers Works, Deepwater, N.J.

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Pollution liability insurance policies have evolved into even more industry specific coverages.

Slag Control in Rotary Kiln Incinerators
Besides causing operating problems in rotary kilns, slag also may fail the EPA’s TCLP for characteristic or listed wastes. The ideal situation would involve the controlled generation of slags that are stable enough to use as fill and construction materials instead of slags that need to go to a landfill.

Pollution Liability: Are You Covered?
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