Application of Sauereisen's Acid-Resistant Refactory
LONG ISLAND LIGHTING CO.’S Northport Unit No. 1 has a 600-ft (183-m) high, reinforced chimney. It is equipped with an independent brick liner. The chimney was constructed in 1966 to serve a 387,000-kW oil-burning boiler unit.

The outer-reinforced concrete column is designed to resist environmental loads, such as wind and weather, but it has little chemical resistance. The outside diameter of the chimney is 24 ft-5 in. (7.4 m) at the top and 49 ft-3 in. (15 m) at the base outside. The wall thickness tapers from 25 in. (0.6 m) at the base to 8 in. (0.2 m) at the top.

The independent brick liner is of lightweight construction, designed to provide acid and chemical resistance. It is constructed of type “H” acid-resistant, double solid brick, laid in acid-resistant mortar. The inside diameter tapers from 25 ft-7 in. (7.8 m) at the base to 16 ft-9 in. (5.1 m) at the top inside. The wall thickness tapers from 20 in. (0.5 m) at the base to 8 in. at the top.

There are two flue openings that enter the lining 34 ft-6 in. (10.5 m) above grade, 120 degrees apart. A buckstay system reinforces the brickwork throughout this section, and lining bands reinforce the liner brickwork throughout the remainder of the lining height.

The stack typically receives a water wash, inspection, and minor repairs on an annual basis. The top 327 ft (100 m) of the lining was replaced in 1986 and was generally in very good condition except for a few minor vertical hairline cracks in the top few feet. The lower 273 ft (83 m) of the liner had numerous vertical stress cracks, spalled brick, and open mortar joints. As a result, a liner sealing and crack repair system was needed. Rather than rebuild the flue, the owner chose a lining system that would eliminate the cracking and spalling problem.

The repair contractor developed a steel, stack-type gunite system using a two-coat process, consisting of a thin pliable membrane covered by a thick gunite layer. The intent of this system was to apply a coating that would:

- Provide a vapor-tight barrier to protect the bricks.
- Protect the anchors that support and reinforce the refractory.
- Fill in the cracks.
- Lower the thermal load on the bricks.
- Reduce the tendency of the brickwork to develop new cracks.
- Increase gas exhaust velocities by maintaining a higher gas temperature. Because of the anchoring system and similar coefficients of expansion between
the substrate (brick liner) and the coating system, the life of this coating is expected to exceed 12 years, more than three times the life of a typical unreinforced “flush coat” system.

The membrane is unique because it is an asphalt mastic, as compared to the normally used urethane. The gunite used is also unique in that it is of low density and thereby ~27% lighter than standard gunite.

**Material Selection Criteria**

The material selection was made after reviewing the operating conditions. Factors considered included both the dead load of the lining system and thermal loading on the brick. While the structural integrity of the brick flue was judged to be sound, the owner wanted to keep the additional dead load to a minimum. Thermal considerations indicated that if the temperature on the brick could be reduced, then the tendency for crack propagation would be reduced. It was decided to use a combination of high-temperature membrane and thermally insulating, acid-proof refractory.

Thermal calculations were run using a computer model. It was determined that a lining of 2 in. (51 mm) of a 98-lb/ft³ (1.6 g/cm³) refractory with a thermal conductivity of 3.2 BTU-in./h/ft²/°F would provide the requisite properties. These calculations were run at a worst-case scenario of 120°F (49°C) ambient temperature and a wind speed of 0 mph. The decision to use a thickness of 2 in. was based on both thermal considerations and dead load. Table 1 gives the physical and thermal properties of various potassium silicate refractories.

The combination of the organic membrane topcoated with the acid-proof refractory was chosen to seal the existing cracks and prevent further moisture absorption by the brick. In this manner, the factors that contributed to the crack development in the first place were eliminated.

The refractory and the membrane combination hinged upon not only the above physical parameters, but also upon chemical considerations. Both components of the lining system had to resist the expected chemical environment. Table 2 shows the anticipated concentrations of sulfuric acid (H₂SO₄) that would condense within the stock at various temperatures.

**Lining Materials**

Prior to the introduction of heat recovery and flue gas scrubbing, the standard lining materials were calcium aluminate-bonded refractories. These refractories were gun-applied over an anchoring system directly onto the substrate. After 1974, when fossil fuel costs made heat recovery not only feasible but also desirable, and the increasingly strict air pollution requirements made scrubbing more common, these refractories proved to be unsuitable. Calcium aluminates form hydraulic bonds according to Equation (1):

\[3(\text{CaO} \cdot \text{Al}_2\text{O}_3) + 12\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \]  

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard Gunite</th>
<th>Lightweight Gunite</th>
<th>Structural Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (pcf–dry)</td>
<td>125</td>
<td>112</td>
<td>144</td>
</tr>
<tr>
<td>Max. service temperature</td>
<td>1,250</td>
<td>1,600</td>
<td>1,400</td>
</tr>
<tr>
<td>Compressive strength 1 day</td>
<td>1,600</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Compressive strength 7 days</td>
<td>2,400</td>
<td>2,600</td>
<td>4,100</td>
</tr>
<tr>
<td>Modulus of rupture (psi)</td>
<td>600</td>
<td>1,000</td>
<td>1,000</td>
</tr>
<tr>
<td>Modulus of elasticity (psi)</td>
<td>5.3 × 10⁸</td>
<td>1.0 × 10⁸</td>
<td>1.97 × 10⁸</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Thermal expansion (in./in./°F)</td>
<td>7.0 × 10⁻⁴</td>
<td>2.3 × 10⁻⁴</td>
<td>5.6 × 10⁻⁴</td>
</tr>
<tr>
<td>Thermal cond. (Btu/in./h/ft²/°F)</td>
<td>6.33 – 5.44</td>
<td>3.18 – 3.2</td>
<td>N/A</td>
</tr>
<tr>
<td>Weight/ft² at 2 in., cured (lb)</td>
<td>19.2</td>
<td>13.7</td>
<td>22.5</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Temperatures °C</th>
<th>Approx. % Concentration by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>0</td>
</tr>
<tr>
<td>57</td>
<td>40</td>
</tr>
<tr>
<td>66</td>
<td>50</td>
</tr>
<tr>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>93</td>
<td>65</td>
</tr>
<tr>
<td>107</td>
<td>71</td>
</tr>
<tr>
<td>121</td>
<td>75</td>
</tr>
<tr>
<td>149</td>
<td>80</td>
</tr>
<tr>
<td>204</td>
<td>90</td>
</tr>
<tr>
<td>260</td>
<td>98+</td>
</tr>
</tbody>
</table>

There are other reactions and products formed, but they all contain the same component elements in varying ratios. These systems react with F⁻, Cl⁻, and all acids. The reaction with F⁻ and Cl⁻ proceeds regardless of pH. Fluorine reacts preferentially with the calcium oxide (CaO) to form calcium fluoride (CaF₂). Chlorine reacts with both the CaO and the aluminum oxide (Al₂O₃), forming calcium chloride (CaCl₂) and aluminum chloride (AlCl₃), respectively, both of which are water soluble and leachable. In the presence of F⁻, there is also some formation of aluminum fluoride (AlF₃), but the Ca-F reaction dominates. These reactions destroy the calcium aluminate binder. In the presence of H₂SO₄, CaO reacts to form calcium sulfate (CaSO₄) 2H₂O, a growth salt. The subsequent hydration of CaSO₄ causes an expansion within the matrix,
As calcium aluminate-bonded refractories lose a significant percentage of their compressive strength after exposure to these environments, their other mechanical properties decline as well. This also applies to other tests in the same solutions at other concentrations. The rate of attack of $H_2SO_4$ is also concentration-dependent. The attack is much more rapid with increasing temperatures.

Potassium silicates are better than calcium aluminate for acid service. Even when attacked by the media, the extent of attack is less severe. Hydrofluoric acid ($HF$), above 400 ppm, is one of the few acids that will attack potassium silicates. Increasing the acid temperature will not cause attack on the potassium silicates except in fluoride-containing acids.

Because of the damage to calcium aluminates, the industry turned to sodium silicate-bonded refractories. These effectively handle very low concentrations of HF and hydrochloric acid (HCl). They tend to have problems in wet $H_2SO_4$ environments, however, because of the formation of another growth salt—sodium sulfate ($NaSO_4$). In addition, the wetter operating environment leads to a higher absorption of acids by the refractory.

Potassium silicate-bonded refractories and sodium silicate-bonded refractories are examples of cements formed by acid-base reactions. These materials consist of a solution of silica dissolved in a strong alkali, either potassium hydroxide (KOH) or sodium hydroxide (NaOH), respectively. The alkali serves to stabilize the solution and prevent the silica tetrahedra from aggregating and undergoing polymerization.

The introduction of acidic species disturbs the electrical charge balance and causes the precipitation of an alkaline salt and the polymerization of an adhesive form of silica as follows:

$$aK_2O \ bSiO_2 \ cH_2O + HX(\text{Lewis acid})$$

$$KX + (\text{SiOH}_4)^n (\text{silanol intermediate})$$

The silanol intermediate dehydrates in the presence of acids or heat to yield the silica polymer:

$$aSiOH_4 + HX (\text{SiOH}_3)_n$$

In going from the dihydrate to the decahydrate, a 12-fold volumetric expansion occurs. This expansion causes stress...
relief within the matrix, cracking and spalling, and the eventual destruction of the refractory.

To overcome these deficits, the power industry has today standardized on a unique combination of materials that overcomes the aforementioned problems. The system employs a multicomponent lining consisting of an organic membrane, resistant to strong acids and temperatures to +300°F (+147°C), which is then top-coated with a potassium silicate bonded refractory that resists the acids present and temperatures up to 1,250°F (670°C) or higher. A further enhancement is the development of thermal-insulating, acid-resistant refractories based on potassium silicates with higher temperature resistance. Thus, by selecting different acid-proof refractories, by varying the thickness of the refractory over the organic membrane, or by combining two or more acid-resistant refractories, it is possible to seal and protect the substrate up to 1,600°F (862°C). Table 3 shows the temperatures and chemical resistance of potassium silicate and calcium aluminate.

Used together, the membrane/monolithic dual lining system overcomes the inherent weakness of each component, and thus offers the user an economical approach to corrosion protection. Neither the membrane nor the monolithic alone can provide a system that will prevent attack on the substrate. Combining the two materials in a properly designed and installed system affords the required protection.

While each case needs to be considered individually, Tables 1 through 3 present some examples of what can be accomplished with these materials.

**Application**

The lining system was installed during April and May 1991. Prior to installing the repair system, the interior of the brick liner was sandblasted to remove fly ash and other contaminants. Anchors were then set in the brick on 8- to 10-in. (203- to 254-mm) centers in a diamond pattern. Following the installation of the anchors, two layers of the high-temperature membrane were installed over the brick and anchors. Airless spray equipment was used in the placement of the membrane. After the membrane cured overnight, the acid-proof refractory was applied over it by gunite at a thickness of 2 in.

**Results of Field Inspections**

After more than 15 years of operating experiences, the lining system is performing as designed. The efflux of acidic gases through the lining has been prevented. The stack is inspected annually.

In recent years, one of the most common maintenance needs for these types of stacks is to address their foundations. Because of the acidic environment, potassium silicate materials are frequently specified. One of these is a castable polymer concrete with more than 4,000 psi (28 MPa) compressive strength, making it appropriate for horizontal applications.
where greater loads exist.

Maintenance applications using polymer concrete proceed rapidly, as the material is easy to prepare with continuous mixing equipment prior to pouring into place at a thickness of several inches. The chemically setting material fully cures much faster than standard Portland concrete. Polymer concrete installations are also accomplished at a much faster rate than bricklaying. This method of maintenance has been used extensively in many recent projects.

Summary

Based upon the success to date, the membrane/monolithic lining system illustrates a solution for rebuilding and maintaining brick stacks. Utilities have neither the available funds nor the time necessary to tear down a liner and rebuild it. In addition, their experiences with thin “flashcoats” of refractory cements have been unsatisfactory because of their short service life. Concerns with block systems can be avoided. With the repair system described, stack owners can effectively rehabilitate their stacks without a prolonged outage, at a reasonable cost and in an environmentally responsible manner.

Reference

1. Data derived from Sauereisen Technical Files (Pittsburgh, PA: Sauereisen).

Bibliography


GARY R. HALL is the manager of organic technology at Sauereisen, Inc., 160 Gamma Dr., Pittsburgh, PA 15238. He is responsible for product development at the company, where he has worked for 38 years. His primary areas of emphasis have included cement technology, corrosion control, and polymer science. He is a graduate chemist from the University of Pittsburgh, is past chair of the NACE Pittsburgh Section, and has authored numerous MP articles. A 32-year member of NACE, Hall has twice been honored with editors’ awards for his corrosion articles in industry journals.

C. KARL SAUEREISEN is vice president and director of Sauereisen, Inc. He joined the family business in 1993, working primarily in the areas of operations and marketing. He frequently contributes to professional journals in the fields of corrosion and specialty materials. He completed his masters of public management degree with highest distinction at Carnegie Mellon University. Sauereisen, Inc. was named 2000 Family Business of the Year in Western Pennsylvania and 2006 Industry Leader for Manhole Rehabilitation by the North American Society of Trenchless Technology.