Performance Characteristics of Copper and Coal Slag Abrasives
By John Peart* and Benjamin Fultz, Bechtel Corporation

Abrasives processed from slags have replaced silica sands in many steel fabrication shops because of their low free silica content. Copper smelters and coal-fired electric generating plants are major material sources for these slag products.

The chemical characteristics of the copper slags are dependent upon the mineral content of the ore feed, the processing parameters, the completeness of the reduction process, and exposure to contaminants during and after air or water quenching.

Contamination of Abrasives from Processing
Ore sources that may be predominantly mined for the recovery of one metal may often contain significant amounts of other metals that are commercially recoverable (e.g., lead, zinc, copper, or arsenic) as well as trace compounds of other metallics. Hence, smelter slags may contain unreduced minerals or metals tied up as compounds if the reduction reaction is incomplete in the smelting process.

Copper slags can be either water- or air-quenched (Figs. 1 and 2). Bottom or coal slags are most often water-quenched. Therefore, the purity of the quenching water and the cleanliness of the quenching basins have a significant effect on the cleanliness of the abrasive product.

Secondary copper smelters are also a source of copper slag. These smelters recover copper from scrap copper alloy products such as telephone switching gear, electronic hardware, wrought products, and wire. Such slag may contain alloying elements (e.g., beryllium or iron). Beryllium is toxic, and iron is easily oxidized to rust, which appears as spots on the abrasive-cleaned steel surface.

The heavy metal content of the coal or furnace slags is the result of the trace element content of the coal source. The oxidation process will concentrate these trace metals.

If some of these are radioactive, the...
sulant slag may have a significant gamma activity.

OSHA requirements do not specify maximum acceptable limits of trace heavy metals in abrasives but do establish maximum safe levels in the workers' blood.

Disposal of spent abrasives is governed by EPA Solid Waste Regulations. The trace heavy metals must test below the threshold level in EP Tox or TCLP tests for disposal in landfills. Additionally, one state, California, imposes total maximum heavy metal content requirements for a non-hazardous landfill disposal classification. Some abrasives may have difficulty meeting these California non-hazardous waste classification requirements. The use of a non-compliant abrasive would result in a hazardous classification and high disposal cost for the generator of the abrasive-paint debris. The new Land Ban regulations which require the treatment or stabilization of these wastes, will make this cost even greater.

As stated previously, another major source of slag abrasive contamination is the purity of the quench water and the cleanliness of the holding basin. Contamination from these sources is more prevalent with coal slag abrasives. Coal-fired power generating plants may use their slag quenching basins for receptors of other materials, such as fly ash, solid stack wastes, and scrubber residues. (Mechanical mixing may occur in the quenching pond.) If the slag is not adequately washed before crushing, contamination of the abrasive will result. These types of contaminants do not combine chemically with the slag but retain their own physical form in the mixture. These contaminants are often visible and appear on the abrasive-cleaned substrate as small, colored specks, depending upon their source.

Soluble Salt-Contaminated Abrasives

Soluble salt contaminants are most often of greater concern to the abrasive user because of their greater potential for reducing coating life. Being unseen, they often go undetected. Coal slags from power generating plants located in tidewater areas, which may use high salt content water for quenching because of its availability, are suspect. The salt content of the abrasive from such slag sources should be determined by analysis of their water leachate.

The critical level of residual soluble salts on the substrate that may reduce coating life and the role of abrasives in their deposition is of great interest to those involved in protecting structures from corrosion. The National Shipbuilding and the Federal Highway Administration research programs both have contract studies in progress to enhance our limited knowledge in this area. The results are awaited.

Influence of Soluble Salts on Coating Performance

Soluble salt residues on substrates to be painted have been observed to initiate and accelerate the corrosion of the substrate and to reduce coating performance.

W.C. Johnson found that residual substrate chloride and sulfate salts on steel surfaces strongly attract and accelerate
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continued

Table 2 Abrasive Sources and Test Panel Data

<table>
<thead>
<tr>
<th>No.</th>
<th>Abrasive Source</th>
<th>Panel Nos.</th>
<th>Surface Profile (mils)²</th>
<th>Dry Film Thickness (mils)</th>
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<tbody>
<tr>
<td>1</td>
<td>Chesapeake Specialty Products</td>
<td>1, 2, 3</td>
<td>.9</td>
<td>15</td>
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<tr>
<td>2</td>
<td>Tidewater Marine</td>
<td>4, 5, 6</td>
<td>.9</td>
<td>16</td>
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<td>3</td>
<td>Apache Tennessee 30-50 Copper Slag</td>
<td>7, 8, 9</td>
<td>25</td>
<td>16</td>
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<tr>
<td>4</td>
<td>Apache El Paso 20-50 Copper Slag Quenched</td>
<td>10, 11, 12</td>
<td>3.1</td>
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<tr>
<td>5</td>
<td>Apache El Paso 20-50 Copper Slag Ambient Cooled</td>
<td>13, 14, 15</td>
<td>3.4</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>H.B. Reed Black Beauty</td>
<td>16, 17, 18</td>
<td>3.3</td>
<td>14</td>
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<td>Klenblast All Purpose #1030 Copper Slag</td>
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<td>8</td>
<td>Rocky Mountain Energy All Purpose Copper Slag</td>
<td>22, 23, 24</td>
<td>2.8</td>
<td>15</td>
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<td>Abrasives Mendiola Bayonne, France Copper Slag</td>
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<td>2.1</td>
<td>15</td>
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<td>10</td>
<td>Clean-Blast Tacoma NA II TruGr®16-3 Copper Slag</td>
<td>Petrographic/scanning electron microscope Examination and EDXRF analysis</td>
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<td>11</td>
<td>Barnes Japanese Tuf-Kut 8-12 Copper Slag</td>
<td>Petrographic/scanning electron microscope Examination and EDXRF analysis</td>
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<td>Apache 30-50 Copper Hill, TN Copper Slag</td>
<td>Petrographic/scanning electron microscope Examination and EDXRF analysis</td>
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<tr>
<td>13</td>
<td>Apache 10-50 Copper Slag</td>
<td>Petrographic/scanning electron microscope Examination and EDXRF analysis</td>
<td></td>
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</tr>
</tbody>
</table>

²1 mil = 25 microns

water transmission through the paint film, due to osmotic pressure, resulting in premature coating failure. Johnson also dis-
cusses how salts cause deposition of mois-
ture on the surface of the steel before paint

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application even though substrate temperatures are above the dew point. This condensation results from the lowering of water vapor pressure by the salt residue at the air-substrate interface.

Rapid evaluation of the degree of water-soluble ion contamination of abrasives can be easily accomplished by measuring the conductivity of their water leachate. ASTM has developed a standard test method, ASTM D 4940, to determine this. The analysis is performed on the leachate from equal volumes of abrasive and reagent grade water. This specification standardizes the method of analysis, but it does not propose an acceptable level of soluble salts for abrasives. A method note is included that defines 500 micromhos per sq cm (microsiemens) and 50 micromhos per sq cm (microsiemens) conductance measurements as high and low soluble salt-containing abrasives respectively. Johnson also proposes 3 categories of concentration ranges based upon leachate conductance testing of commercially available abrasives.

Both the Navy Specification, MIL-A-22262A (SH), and the proposed Steel Structures Painting Council abrasive specification establish maximum acceptable leachate conductance levels, but they have been promulgated on water/abrasive ratios that differ from the ASTM method.

Table 1 is a comparison of ASTM, US Navy, SSPC, and Johnson’s proposed limits of conductivity reported in microsiemen normalized to represent leachate from equal volumes of abrasive and water.

As can be seen from this variation of the proposed requirements, no uniformly accepted standard exists. It should also be noted that all the limits in Table 1 were arbitrarily established and are not based on controlled testing to establish critical limits (i.e., the critical ion concentration at which premature coatings failure occurs).

Objectives
The objectives of the study were three-fold:
- to determine the ion concentration of water leachates from representative abrasive blast media supplied to the US shipbuilding industry,
- to determine if any of the abrasives cause rapid rust-back (flash rusting), and
- to determine if any of the abrasives cause blistering of paint films in immersion service.

Coating Test Design
Six copper slag and 2 coal slag abrasive products from 6 different suppliers were selected for evaluation. A G-40 steel grit was used as a control.

Triplicate six-inch (15-centimeter) by six-inch (15-centimeter) panels were blast ed to SSPC-SP 5, White Metal, using each test abrasive and the G-40 steel grit control for a total of 27 panels. All the panels were cut from the same piece of new, 1/4-inch (six-millimeter) thick, A-36 steel with intact mill scale. Two panels from each set were coated with the VOC-compliant version of the US Navy Formula 150/151 epoxy coating system. The resultant dry film thickness of the two-coat systems ranged from 14 to 16 mils (350-400 microns). See Table 2 for a list of abrasives tested, profile, and actual dry film thicknesses of each

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Samples of each abrasive product in the as-received condition were collected and retained for the determination of pH, conductance, and soluble salt concentrations of the leachate. Conductance and pH were measured in the laboratory, using laboratory equipment, and in a field environment, using hand-held, pocket instruments. The pH was also measured using a "Chemetrics Vacuette" colorimetric field test. Leachable chloride concentrations were measured using both field and laboratory equipment. Leachate sulfate concentration was determined by laboratory analysis only.

After being abrasive blast-cleaned, the uncoated panels were placed in a controlled environment and observed for rust-back during a period of 7 days. Pictures were taken at regular intervals. Ambient relative humidity varied from 55 to 70 percent, and temperature varied from 70 F to 75 F (21 C to 24 C).

Coated panel sets were placed in 2 different immersion test environments. One set was tested in distilled (DI) water in a pressure chamber at 100 F (38 C) for 1000 hours. The pressure of the chamber was maintained between 52 and 55 psig.

In the second test, coated panels were immersed in DI water for 6 months. The DI water was at ambient temperature condition for the first week of exposure. It was then changed, and the replacement water was maintained at 82 F (28 C) for 30 days. The DI water was again replaced, and for the second 30 days of immersion, the DI water cycled at 82 F (28 C) for 5 days, then at 120 F (49 C) for 8 hours for 2 days. This resulted in 64 hours of immersion at 120 F (49 C).

For the next 4 months, the DI water was maintained at ambient temperature, which ranged from 76 F to 90 F (24 C to 32 C).

Rust-Back/Blistering Test Results
No rust-back was noted after 7 days on any test panels cleaned with abrasive or the controls, which were cleaned with new, degreased G-40 steel grit.

None of the painted surfaces prepared by the test or control abrasives showed rusting or blistering in either the ambient or 50 psig pressured distilled water immersion tests.

Both the ambient pressure, deionized water test at 120 F (49 C) and the pressurized deionized water test are harsh in nature. They are effective indicators of film integrity and the presence of critical concentrations of contaminants that induce osmotic pressures and accelerate moisture transfer through the paint film.

Leachate Analysis
All analyses were performed on a water leachate prepared using equal volumes of test abrasive and reagent grade water.

Table 3 contains a compilation of the laboratory and field measurements of sulfate, chloride levels, and leachate conductivity. Units of conductance are listed in microsiemens.

Mineralogical Examination
In addition to coating flash rusting, several copper slag abrasives were selected for...
mineralogical examination and the scanning electron microscopy and energy dispersive x-ray analysis (SEM-EDXRF). The results are summarized below.

- Sample No. 10—No metallic copper was observed. SEM work shows traces of combined copper in a few slag particles. This copper may, however, be associated with copper-bearing sulfides and/or secondary copper minerals that formed after the slag production.

- Sample No. 11—This sample contains noticeable amounts of metallic copper (Fig. 3). In addition, there are secondary copper minerals (probably malachite). The metallic copper is alloyed with approximately 10 percent iron (semi-quantitative SEM-EDXRF analysis).

- Sample No. 12—No metallic copper was observed. SEM-EDXRF work shows traces of combined copper in a few slag particles.

- Sample No. 13—The slag particles of this sample appear to contain appreciable amounts (greater than 2 percent) of residual sulfides from the ore, some of which was copper-bearing. Metallic copper was not detected.

The Japanese product (Sample No. 11) in Fig. 3 was the only abrasive examined that contained notable amounts of metallic copper. It was alloyed with approximately 10 percent iron. In addition, there was a secondary mineral present, most likely malachite. The material is no longer being marketed in the US and was not available to be included in the performance testing or leachate analysis.

The slag source from which the abrasive was produced could not be identified. The other products examined contained no free copper, but trace amounts of copper were present in a combined form. These products did not cause rust-back or reduced coating performance as documented by the test results obtained in this study.

Conclusions

The abrasives tested did not produce flash rusting or reduced performance of the Navy Formula 150/151 low VOC epoxy coating system in the ambient or the pressurized deionized water immersion. Equal volume abrasive/water leachate conductance levels in the 0.550 microsiemens range did not adversely affect the performance of the coatings system tested.

The exposure environment history and the degree of contamination of the surfaces being blasted appear to have a more critical impact on the concentration of residual salt on the cleaned substrate than the concentration of ionic constituents in the process abrasive. Field instrument measurements of abrasive leachate conductance correlate well with more sophisticated laboratory instrumentation. Their use in conjunction with ASTM D 4940 provides a fast, accurate, and reproducible method to determine the degree of ionic contamination of the abrasive product being used.

Metallic copper was identified in only one of the copper slags examined. The material is no longer marketed in the US. The other copper slag abrasives examined contained traces of combined copper; however, subsequent accelerated corrosion testing did not indicate any resultant ill effect on coating performance.

No correlation between copper content and rust-back or blistering was observed, nor did the test results substantiate the copper disposition-anodic site initiation theory of rust-back postulated by the Mare Island report.2

Summary

The steel fabricator and the owner of the structure are concerned with the quality of the applied paint system and want assurance that it will perform effectively to control corrosion and steel loss for its predicted life.

The quality and cleanliness of the abrasive used in the surface preparation process have a significant impact on the coating system performance. Therefore, abrasive procurement specifications must reflect objective requirements that characterize available products that will produce the required substrate for a quality coating application.

In addition, the fabricator requires not
only a quality abrasive product but also competitive sources of supply.

If unrealistic material specification requirements are promulgated, based on inadequate data or conjecture, some competitive sources are eliminated, and surface preparation and painting costs escalate significantly.

In response to this issue, this study characterized 8 commercially available copper and coal slag abrasives for water-soluble contaminants capable of being transferred to a clean substrate. The study evaluated the effect of the abrasives on coating performance.

It was determined that the 8 products tested produced acceptable substrates for the application of coatings for immersion service.

Petrographic examinations, scanning electron microscopy, and energy dispersive x-ray analysis identified copper compounds in 3 copper slag abrasive products marketed in the US. Test results determined that these compounds had no adverse effect on subsequent coating performance.

The study results did not support the rust-back and blistering phenomenon reported by the Navy Mare Island Paint Laboratory investigation. Nor did the results confirm the theory concerning rust-back due to the development of free copper cathodic sites on the substrate. The findings of the Mare Island study were the primary data on which the Navy based many of the requirements of specification MIL-A-2226A (SH) for abrasives.

Acknowledgments
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Dr. Wolfgang Baum, Pittsburgh Mineral and Environmental Technology (PMET), performed the scanning electron spectroscopy (SEM) and energy dispersion x-ray analysis.

References

Transportation Departments Surveyed for Coatings Specifications
By Robert Kogler and William Mott, Ocean City Research Corp.

In 1988, as part of a seven-year research project funded by the Federal Highway Administration (FHWA), the Ocean City Research Corporation (Ocean City, NJ) conducted a survey of the 50 state departments of transportation (DOTs). This survey assessed the current generic types of coating systems used by the various states for corrosion protection of steel bridge structures. The results of this survey were used to assist in the development of a test matrix for an FHWA-sponsored program evaluating environmentally acceptable bridge coatings.

The state representatives contacted were asked to name the primary coating systems used in their state for both new construction and maintenance painting. The results represent the coating systems used or recommended by the state DOTs in the majority of their painting operations. Coating systems used under special circumstances by any of the states were not considered. Where certain states reported more than 1 primary system, all the systems named were included as primary systems in the

Fig. 1
Primary coating systems of state transportation departments for new construction

Fig. 2
Primary coating systems of state transportation departments for maintenance painting