Carbon—Something Old, Something New

Processing requirements for carbon-based products are as variable as the allotropic forms of carbon itself.

Graphene super-capacitors might someday enable electric cars to be fueled more quickly. ***(Photo copyright © Chevrolet.)***

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Carbon is one of the earliest known elements. It was used by the Egyptians and Sumerians in the form of charcoal around 3750 B.C. for the reduction of copper, zinc, and tin ores in the manufacture of bronze.[1] Carbon is one of a handful of elements that exist in multiple forms due to its allotropic nature. Carbon's diversity is evident in the two more common forms: diamond, the hardest natural mineral; and graphite, one of the softest minerals.

Carbon's unique chemical and physical properties allow its use in a wide array of products. Carbon is broadly used for energy (coal), pigments/colorants, metallurgy and plastics. Diamond is not only used for engagement rings, but also in many industrial cutting devices due to its hardness. Graphite has many uses—in pencil lead, as a lubricant, in steel and aluminum manufacturing, electrodes, cathodes, brake linings, fuel cells, batteries, and refractories.

The bulk of natural graphite supply comes from China—more than 75%.[3] Demand is growing within China for use in steel refractories, pebble bed nuclear reactors and lithium-ion batteries, which are limiting global supply. The global supply of natural graphite exceeds 1.3 million tons.

The U.S. does not have any appreciable natural graphite supply, and therefore it produces a significant amount of synthetic graphite. Over 1.65 million tons of synthetic graphite are produced annually.[4] Synthetic graphite provides superior consistency and purity but can cost 10-20 times that of natural graphite. Synthetic graphite is manufactured by converting other forms of carbon (e.g., needle coke and coal tar pitch) into graphite at ultra-high temperature.

Future Possibilities

Relatively recent developments include the inclusion of carbon in lithium-ion batteries that are lighter and more powerful. These batteries require as much as 10 times more carbon than lithium in the manufacturing process. Future uses of graphite include applications for enhanced safety in the nuclear field, such as bed reactors that are fueled by uranium encapsulated in graphite.

The potential of recently discovered graphene, referred to as a super material, seems boundless. The thinnest material known to mankind, graphene is exceedingly strong (200 times stronger than steel), lightweight and flexible. It is also exceptional at conducting electricity and heat, and at absorbing and emitting light.[2]

An article published in the journal *Science* details the work of researchers at UCLA who are working on developing graphene super-capacitors that will enable electric cars to be fueled in a minute at a recharging station. "Our study demonstrates that our new graphene-based super-capacitors store as much charge as conventional batteries, but can be charged and discharged a hundred to a thousand times faster," said Richard B. Kaner, professor of chemistry & materials science and engineering.

Back to the Present...

Conventional carbon products are critical to many industries, especially carbon electrodes for steel production. The thermal processing requirements of these products are well-defined, but the degree of sophistication required for successful firing systems is significant. Some of the design challenges for the furnace include:

- A wide range of BTU input due to highly variable heating rates
- Potential condensation within the refractory linings must be prevented; the evolution of volatile hydrocarbons and sulfur gases can create havoc with the insulation anchoring system, as well as the steel casing
- Management of the firing system to provide excellent temperature uniformity with limited burner convection
- Ability to properly cool the product without the use of cooling air
- Maintain security of operation in the furnace during volatile evolution while it is filled with combustible gases; air-tight furnace construction is imperative to exclude any ambient oxygen from entering the furnace and spoiling the < 2% O_2 environment
- Exhaust gas pollution treatment is required to eliminate VOCs, as well as SO_x compounds

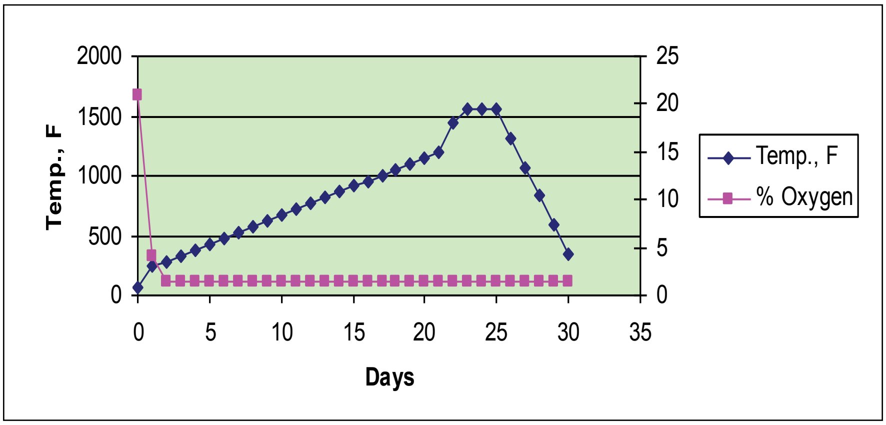

Figure 1. Sample carbon firing cycle.

These are difficult requirements, but they are all crucial to the successful thermal processing of these types of carbon-based materials.

Optimizing Production

Several different baking processes are required to manufacture carbon products, but a sample cycle appears in Figure 1. The extraordinarily slow initial heating rates are required because the products are normally encapsulated in large SiC saggars. Consequently, heat is transferred to the carbon parts by conduction only; to avoid temperature non-uniformity within the product, rates of heating are necessarily slow—as few as 2ºF/hour.

In addition, because of the massive payloads within the furnace (up to 1 million pounds of product) the heating system requires considerable input to perform the final heating segments. Therefore, careful selection of the burners (i.e., wide range of input capability), as well as specialized control (e.g., high-low or high-off pulse), is essential. The burner sequence of pulsing is also crucial in developing the best possible results. Burners selected must be ultra-high-velocity to maintain adequate temperature uniformity without the use of excess air. In some cases, auxiliary recirculation fans are used to supplement the convection currents developed by the burners.

In conventional kilns, the products of combustion include CO_2 and H_2O (water vapor), and the water vapor permeates the refractory insulation. In carbon firing applications, various VOCs migrate through the kiln lining and condense, only to literally catch fire during different periods of the firing cycle if oxygen is present. To eliminate the condensation, vapor barriers are installed within the refractory insulation, and are strategically placed so that these vapors do not condense.

NFPA 86 requires that furnace atmospheres be maintained well below the lower flammability limit (LFL) for secu-

These kilns can be enormous, firing 1 million pounds of product per cycle.

rity of operation. In carbon baking, the opposite is true: the furnaces are operated well above the upper flammability limit (UFL) to avoid uncontrolled combustion incidences. This means that the burner system has to be set up and controlled at near stoichiometric ratio in order for the atmosphere inside of the furnace to be < 2% oxygen. In this environment, even though there is free hydrogen and carbon monoxide, no spontaneous combustion can take place because the environment is well above the UFL. This requires the furnace to be literally air tight, despite having a door system, as well as a kiln car. Patented sealing devices for the kiln car/seals, as well as the door system, are effective means of meeting this requirement.

Cooling the massive payloads in these furnaces is another area where conventional cooling methodology is not applicable, because of the low O_2 requirements. Accordingly, the use of water to gas heat exchangers, or direct cooling through H_2O injection, is required. The water injection technique is the most economical, but the control algorithms for this technique to be successful are critical.

Last, when firing these products with a large organic component, environmental requirements must obviously be observed. Since these components can exceed 25% by weight, the CO, particulate matter, and SO_x levels in the kiln exhaust are significant. Accordingly, thermal oxidizers are normally applied at the kiln exhaust, combined with downstream SO_x wet scrubbers, to ensure that air emission requirements are met. Presently, the design challenge requires large ceramic or specialty alloy valve systems that govern exhaust gas flow paths and pressure control systems.

New/Old: Still a Great Material

Carbon is a material with almost infinite use and capability. Some of the current discoveries and uses may be disruptive technologies that can truly change everything. Yet traditional uses of carbon will continue to endure in the foreseeable future because of the material's usefulness under extreme conditions. Processing requirements for these materials are as variable as the allotropic forms of carbon itself.

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