Clearing the air: Gas grief goes with new Selee filter

By Peter Wray

ACerS 2009 Corporate Environmental Achievement Award winner

A call from an a magnesium–aluminum alloy manufacturer that came into Selee's headquarters early in 2006 was surprising, if not alarming. The customer wanted to know if Selee had ever heard of one of its ceramic filters igniting, because that's what the alloy maker just experienced.

Now, on its face, the idea that one of these filters could catch on fire is a little far-fetched. The main component of the filters, phosphate-bonded alumina, isn't flammable.

Even more to the point, the entire purpose of these filters would suggest that the filters couldn't ignite. Selee's filters play a key role in the production casting of metals, such as aluminum, iron and steel as well as their alloys. After the raw and recycled materials for the metal are combined and raised to molten temperatures, the metal flows down a trough into a special square bowl which holds one of Selee's preheated ceramic filters. Gravity then pulls the molten metal through the filter. Nonmetallic inclusions, such as aluminum oxides and spinels, are undesirable in the finished product, and the filter acts to remove these inclusions from the melt.

The filter – made of custom size and composition for each application – purifies the molten metal by chemically and physically binding inclusions as the metal passes through the filter. After passing through the filter, the metal then continues down another trough until it is ultimately formed into an ingot, billet or rolled product.

After each batch or "cast" of metal is processed and the last of the metal is drained, the filter commonly is replaced by abrading a hole in the ceramic and lifting it out with a crane. A typical cast might last an hour or two.

Thus, if the filters were going to ignite, one would think they'd have plenty of chances to do so, either during the preheating stage (accomplished with a gas torch) or while filtering the hot metals (ranging, for example, from 600°C to 1,600°C).

In fact, the customer reported that the ignition occurred well after the spent filter had been removed. The problem took place while the customer was cutting up the filter. As is often the case, metal makers are interested in looking at what the filter caught, what's retained in the filter and what kind of inclusions are trapped. This type of data gives them insights about what's happening upstream in their metal.

To do this, customers section a filter and then closely examine and test the pieces to see what inclusions have been captured. In this particular case, the customer reported that its workers had cut up the filter with a wet saw.

"We got all the particulars of that application from the customer and tried to duplicate it here in our lab," said Watt Jackson, Selee's vice president of sales and marketing, "but we weren't able to reproduce the ignition. But as part of our analytical process, we measured the gasses that were released from that spent filter after cutting. To our surprise, we found the presence of phosphine gas."

Not to be confused with phosgene, the "mustard gas" of WWI infamy, phosphine gas (phosphorus trihydride) is still nothing to be trifled with. It is highly toxic, odorless, can be lethal in low concentrations and is often used to control rodents on farms (sold as a phosphide that is converted into phosphine when exposed to moisture in the atmosphere or stomach).

ACerS 2009 Corporate Environmental Achievement Award

The Society established its Corporate Environmental Achievement Award to recognize and honor a single outstanding environmental achievement made by an ACerS corporate member in the field of ceramics.

These achievements represent either

- A significant improvement of an existing process or product, or
- The development and implementation of a new process or product.

In both cases the process and/or product should demonstrate improvements in one or more of the following areas:

- Reduction in undesirable effluent streams;
- Expanded recycling of materials; and
- Measurable environmental benefits over previously established processes.

Details of the technology and product commercialization are presented at a special technical session during MS&T events. This year, Rudy Olson, representing Selee – winner of the 2009 CEAA – will make a presentation on Selee's award-winning CS-X filter technology at 8:00 a.m. on Tuesday, Oct. 27, in the David L. Lawrence Convention Center in Pittsburgh, Pa, as part of ACerS' Emerging Opportunities for Ceramic Science and Engineering Session.

Rudy Olson led the Selee team that created the environmentally friendly CS-X filter.

Pioneering foam filters

This was a surprising development for a company that had been making ceramic filters for more than 30 years. Selee, originally a division of aluminum producer Alusuisse, invented ceramic foam filters in the 1970s. These filters were a big improvement over the deep-bed filtration technologies that had been in use, which depended on filling a large vessel with alumina balls. The process was bulky and unpredictable to the point that metal producers couldn't detect filter failure until metal quality started to degrade – perhaps in the middle of a cast. The ceramic foam filter, on the other hand, is small and designed for one-time use. It is a cast and toss process, so to speak.

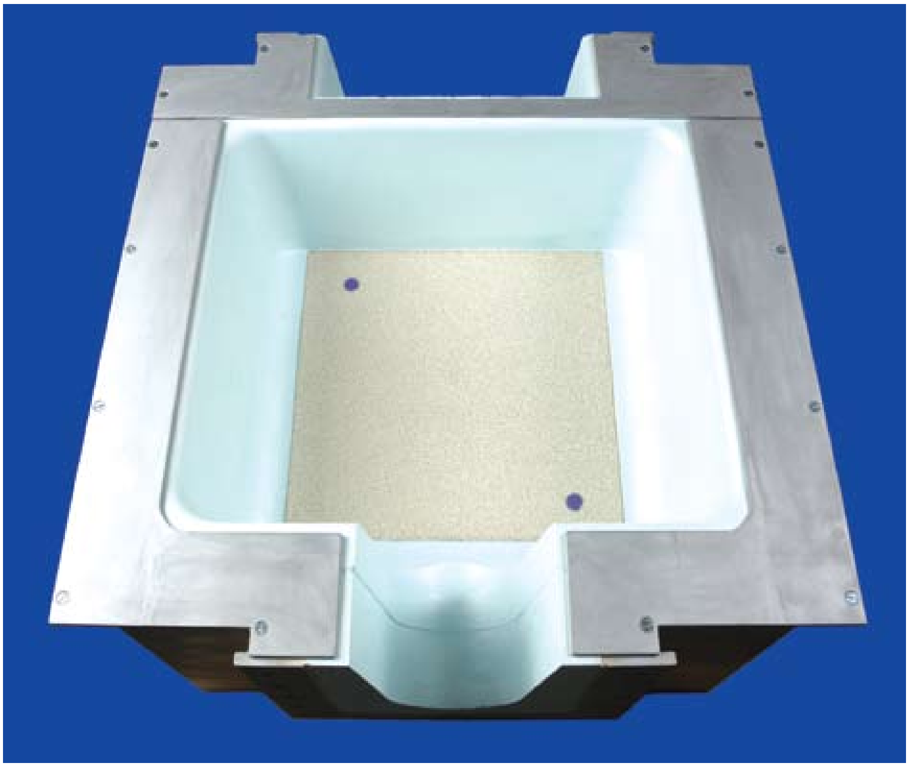
Although the phosphate-bonded alumina filters performed well, Selee was also selling to Alusuisse's competitors. This situation, combined with Alusuisse's assessment that the filters weren't a core technology, led to Selee's eventual spin off. Ultimately, Selee found its home as part of Porvair LLC, a company based in the United Kingdom that has other filtration technologies in its portfolio.

Over the next decades, Selee continued to focus on molten-metal filtration, but looked beyond only aluminum cast houses to opportunities in iron, steel, copper and superalloys, applying the same basic concept of a ceramic foam as a filter media. Standard sizes within the various industries developed. For example, for aluminum makers, Selee could offer products from 9 to 26 inches square. All are 2 inches thick with sides shaped to the bowl's bevel, plus an expandable gasket.

But, Jackson notes that the filters for other metals require important changes. "With iron and steel, the applications are quite different than with aluminum. The iron and steel settings are typically foundries, and the filter sizes are smaller and much more variable. They run anywhere from a few inches square up to 6 inches square and come in three different thicknesses. Instead of a single unit, multiple filters are placed in certain patterns," Jackson says.

"That's where research and development helps," says Rudy Olson, Selee's director of engineering. "Each application requires quite different formulations. In the aluminum industry, the filter needs to be resistant to corrosion and the process is set up much differently. In iron, the common filter is a silica-bonded silicon carbide material. With steel partially stabilized zirconia is required for the filter because the refractoriness and the thermal-shock resistance requirements are extreme."

Jackson says it is important to identify the particular requirements of an application. "We have to know whether the filter porosity should be very fine and, thus, is more efficient in capturing inclusions, or should have larger pores that allow higher flow but captures less of the inclusions. There are several variables that come into play when choosing or designing the right filter for an application," he explains.



Selee ceramic foam filters fit in the bottom of special temperature-resistant bowls during molten metal processing.

The phosphine mystery and the CS-X.

So, after many years without major problems with phosphate-bonded alumina as the filter basic composition, the discovery of phosphine in the filters' offgasses was taken seriously at Selee's North Carolina headquarters. "Phosphine gas is not good for safety and environmental reasons," warns Olson, a member of ACerS. "You don't want to inhale large amounts of it. Environmentally, many times after use the filter ends up in a landfill," where the problem could spread.

Selee researchers started looking at what conditions phosphine gas was emitted from a filter. "What happens," says Olson, "is that magnesium is an excellent reducing agent. Phosphorus is a material that is easily reduced. So, when you are starting with a phosphate binder, that magnesium can easily reduce that phosphate to phosphorus or a magnesium phosphide. When water reacts with the phosphorus, you end up with residual magnesium oxide and phosphine gas which is formed when hydrogen is pulled from the H_2O."

"That obviously made replacing the current formulation in the industry with a nonphosphate-based formulation a high priority," says Jackson.

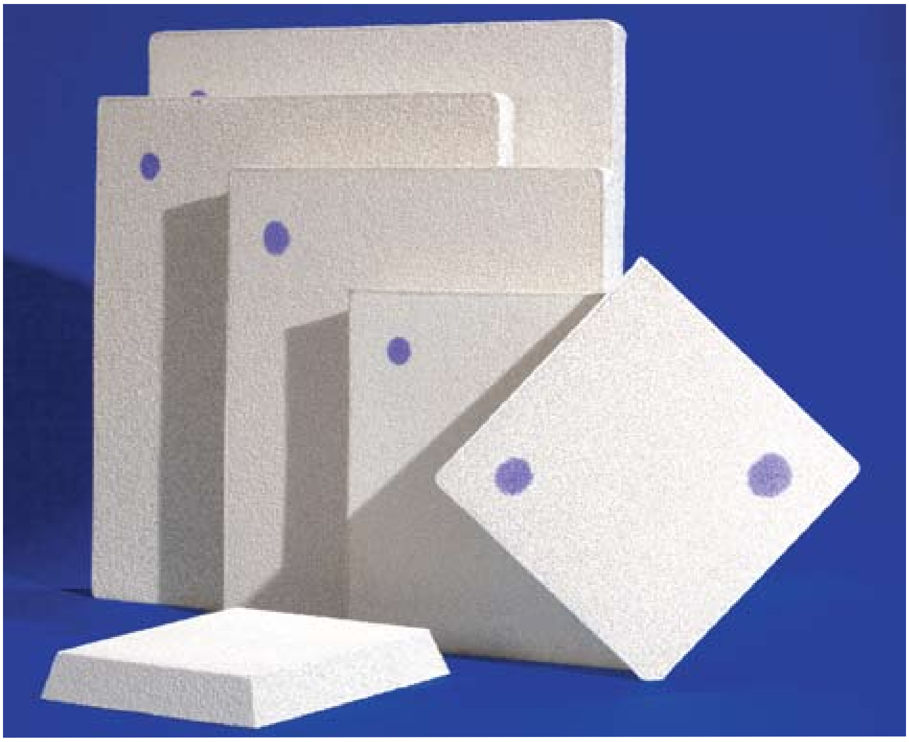
In response, Selee launched an R&D program to find a nonphosphate-bonded alumina formulation so that this reaction could be eliminated. Feng Chi and David Haack, both trained at the University of Texas at Austin, played instrumental roles in the formulation development. Leonard Aubrey, vice president of technology and Case Western Reserve University graduate led metallurgical studies, and Northwestern University-trained Olson led the process development.

In another surprise, Selee discovered during its research that the reaction that occurs to produce the phosphine gas also can result in performance and quality issues.

Jackson said they found out that there was a corrosion reaction occurring in the filter body. "This basically means that filter body begins to break down. When that body begins to break down, the molten metal becomes wetted to the filter body and you begin to have a release of the inclusions that previously have been captured. There is also the potential to have filter particles breaking away from the filter because of edge crushing," he says.

The end result of the R&D effort is Selee's award-winning CS-X filter – a product that solves an environmental issue and works as a better-performing filter.

But Olson says the road to the CS-X wasn't easy. "In the original composition, the phosphate-bonded alumina is largely alumina grain, about 85 per-



Ceramic foam filters come standard square shapes and sizes up to 26 inches. The beveled edges provide a tight fit special filtering bowls.

cent, plus a fraction of phosphate glass that bonds alumina. In the new formulation, it was fairly difficult to find a replacement for that phosphate binder. It turns out that the phosphate binder mechanically is very strong. There is no shrinkage during firing, and it is easy to use. So we had to come up with something that fit all those criteria, and be as good – or better – going forward," he says.

Jackson credits the success to a methodical approach. "We probably went through three iterations of formulations over a year," he says. "There was the first phase which was coming up with the first possibility, and that probably took a year to a year and a half to come up with the first candidate [for a substitute]. Then we went through two to three variations of that before we ended up with a final formulation, and that step took roughly another year."

He also says Selee wanted the changeover to a new filter to be hassle-free for customers. "Any new product had to go across all applications at about the same cost and be a transparent changeover for the customer. They would want to use the same equipment, same operating parameters and same practices. Otherwise, the conversion would take a long, long time," says Jackson.

Olson recalls that they were helped by a good idea for a candidate from the beginning. He says the possible substitute was a material "we had known about for a little while. This occurrence that we had in the field was really the motivation to push forward."

Olson's team ended up with a boron aluminosilicate binder in its new CS-X filter. "It's the properties of that glass that improve the characteristics, and also it is completely phosphate-free.

Watt Jackson, Selee's vice president of sales and marketing.

We did have to change our process to handle this new material, but in the end we ended up with something with improved performance."

Improvements, indeed: The CS-X filter also has improved thermomechanical resistance (reducing the potential for catastrophic failure), retains less metal (less waste) and doesn't contain refractory ceramic fibers. It also satisfies the Registration, Evaluation, Authorization and Restriction of Chemicals regulations in Europe.

Rapid replacement

Selee reports that it quickly converted most of its customers and shipped more than 100,000 CS-X filters in 12 months. About 70 percent of the customers are completely converted, and the balance, who are still completing their internal process to qualify the new filters, should be converted by the end of the year.

"We've been happy with how quickly the customers have qualified the filters, and they seem very happy with them. It's been relatively easy," boasts Jackson.

As with any business that has invested R&D resources in new technology, protecting intellectual property is a big concern, but even on that front, Selee is finding success. Olson says that the company has filed for patents in several countries for the new CS-X filter. "All indications are that it is going very smoothly," says Olson. "We actually received confirmation that the CS-X patent is going to be published in several countries, and everything we are hearing back is very positive, so we foresee that the CS-X filters will have very strong patents in several countries. If we are going to make that R&D commitment, we want to be rewarded for those efforts."

Other members of the CS-X development team included Niki Rhodes, Mark Topolski, Matt Willer, Nikki McGinnis, Brian Ferrand, Mark Heamon, Ramon Duque, Mike Lukens, Trish Steppe, Kim Melvin and Mark Grush; and production team leaders Jess Maybin and James Edgerton, along with the production crew. ■