White Paper:
Developing Thermal Processes with Energy Efficiency in Mind

By Brian Fuller, Sales Engineer
Bruce Dover, Senior Process Technology Engineer

ABSTRACT

Thermal processing is typically the most energy intensive portion of a materials manufacturing process. Opportunities to conserve energy not only reduce ecological impact, but can result in significant cost saving, as thermal processing is a critical cost driver in direct equipment and installed utility requirements. To make the best use of possible opportunities, it is important to consider the form of the commercial process as early as during laboratory development to ensure it will be suitable for application in the intended continuous form. In particular, continuous thermal processes offer multiple opportunities for energy conservation over batch, including reduced residence time, minimizing thermal requirements to heat ancillary process components, and opportunities for use of byproduct materials and heat for preheating. Detailed discussion on opportunities for continuous, energy efficient thermal processing will be provided with examples of commercially relevant processes to illustrate the concept and provide a guide for future considerations.

INTRODUCTION

Material refinement and processing can involve dozens of unit operations to finally arrive at a saleable, high-value advanced material. Thermal processing is typically the most energy intensive portion of a materials manufacturing process. Thermal processing has many opportunities to conserve energy for both cost savings and ecological impact.

Often the link between initial process investigation and the commercial scale production plant is made too late in the process development. For an existing process, every time you want to save energy, you have to put equipment in place perhaps with an unfavorable return on investment. With demands for decreasing time-to-market, realizing a more energy efficient process exists, or worse yet is required for commercial success, needs to occur up front in development. The affect of scaling the process to meet the short term demand of sales and marketing for supplying test quantities of final product to potential customers leads to the trend of batch furnaces with increasing residence time proportional to production size. Frequently these steps are repeated several times and producers tailor their processes to the particular characteristics of the batch product. The residence time should not be ignored; the furnace construction and operation should be considered for each scale up step with the commercial end in mind. With steady, high volume material demand the goal should be continuous over batch processing. Significant energy conservation advantages of continuous thermal processing over batch processing are discussed broadly. Example processes are presented for future consideration.

COMMERCIAL PROCESS

<u>Process Types</u>
The specific starting material and target product place the thermal process into one of several broad types: Calcining and Pyrolysis, Sintering and Synthesis. These process types each have their own thermal requirements which dictate furnace type and construction, and also opportunities for heat recovery. Each type can exist in a wide range of temperature and atmosphere requirements.

Calcining and Pyrolysis processes involve the heat treatment of a solid to produce both solid and gas reaction products. Key processing concerns efficient heat transfer into the solid bed and gas management to control the atmosphere and extract condensable gases. An example of Calcination is the removal of bound water and carbon dioxide as in formula (1) below, whereas Pyrolysis can be the decomposition of a polymer in an inert atmosphere leaving behind carbonaceous solid and condensable gases.

$$Nd_2(CO_3)_3{\cdot}2H_2O \rightarrow Nd_2O_3 + 3CO_2 + 2H_2O \quad (1)$$

Sintering processes most often involve the heat treatment of a part, but may also apply to loosely agglomerated powders, with the goal of increasing the density and strength of the part. Key processing concerns are uniform temperature control and atmosphere control.

Synthesis processes can be solid-solid or gas-solid complex reactions to produce a new solid material. Key processing concerns efficient heat transfer into the solid bed and gas management to control the process atmosphere or volatiles.

Material Flow

For each of these processing types, the flow of the material through the thermal process will gauge which furnace type is possible. How will the material be transported through the thermal processing units? If the material is a powder, low energy advantages exist if the bulk powder is free flowing throughout the process. If the powder is sticky it prevents the use of such high heat transfer and uniform processing units such as rotary tube or vertical tube furnaces. For processing parts, how can they be transferred through the furnace while allowing uniform heating, gas diffusion and shrinkage while optimizing the furnace volume? In both cases where a bulk powder is free flowing and a process part can be arranged in smaller loads with more direct paths to heat transfer and gas diffusion, the benefits are often shorter processing times and a more uniform product.

Commercial Volume

Based on the potential applications for new advanced materials, the markets need to be sized for future commercial plant capacities. The volume of material required at the commercial scale can strongly influence the form of the commercial process. For example, a high temperature process where at the pilot production scale a ceramic tube rotary furnace is suitable for the production capacity, at the commercial production scale a whole new furnace type will need to be implemented. The reason is scalability. The ceramic rotary tube furnace will be limited in diameter and length due to the materials of construction. Knowing the final production rate required will enable thoughtful decisions regarding the furnace configuration.

Maximum Temperature

The maximum design temperature of the furnace, independent of whether or not it is ever operated there, means the manufacturer will use materials capable of continuous operation in that high temperature. The higher the temperature rating of an insulating material is the higher the cost and the lower the insulating properties will be. This is one of the reasons insulating walls are typically thermally graded, with varying composition as you get farther from the hot face. The design of the furnace insulation is not as simple as adding thicker insulation. This increases the furnace volume and cost and also raises the average temperature across a piece of hot face insulation, limiting its useful life. Operating at a relatively high heat flux through the insulation wall gives strength to the refractory, but may require the use of a water-cooled steel shell to maintain the integrity of the furnace. Water-cooling is frequently required for high temperature graphite furnaces. The added treatment of cooling and quality in a closed-loop water cooling system adds to the plant's operating cost. These trade-offs should be considered with the need for operational flexibility and processing various grades of product when specifying the maximum capabilities. A furnace designed for a higher temperature will be less energy efficient.

Product Quality

The source and quality of the raw material has an impact on the number and type of processing steps. Take the extraction, calcination, and separation of rare earth oxides for example. An ore sample with but a trace amount of the target oxide, for example 6 wt-% light rare earth oxides in the Bayan Obo, China deposit[1], is an intensive series of wet chemistry and thermal steps. The wet chemistry steps including the preparation of aqueous solutions, removal of bulk and trace water, and handling of waste water are costly. In addition, these material sources often lead to low yields at thermal treatment. For example a 67% recovery in the ore calcinations from formula (1) above, or even 18-20% recovery in the pyrolysis of rayon fibers[2], means each thermal step is sized for the large volume of incoming feed. If the volatiles are removed at the front of the furnace then only a small volume fraction of the remaining furnace is utilized.

Related, the final target purity and avoidance of detrimental elements for products such as battery and electronic materials quickly limits the process environment. Consider materials for electronic and energy storage applications which demand very low impurities. Trace, large, metallic elements such as iron, nickel and zinc have a detrimental effect by changing bulk electrical properties, promoting side reaction, or changing crystal morphologies. However, the major concern is safety of the battery and avoiding the formation of internal short circuits often caused by crystal growth promoted by the foreign metal deposit from the anode surface to the cathode, penetrating the separator[3]. Limiting the process to non-alloy materials of construction quickly leads to long cycle times limited by slow ramp rates of high mass kiln furniture, or multiple smaller capacity furnaces which are inherently inefficient. A rotary tube furnace with non-alloy process tube has limited tube sizes due to manufacturing materials and techniques. For commercial scale plants making 10 tons per day or larger, this leads to dozens of small rotary furnaces or fewer large footprint tunnel furnaces. Advancements in manufacturing and furnace designs can lower the risk associated with larger diameter quartz process tubes, but ceramic tubes may never be available in larger diameters.

The final purity should be dictated by the end-use application, and sometimes the requirements are unavoidable. Likewise the process atmosphere is often not flexible and dictated by the reaction. A majority of the time a process requires either an oxidizing, inert, or reducing atmosphere. Within each category the specific utility gas to use is important to the overall plant energy footprint. For example, consider a process which needs an inert cover gas: the preferable gas to use is nitrogen, but nitrogen is not always inert. So a safer position may be the use of argon. However, at an average atmosphere composition of 0.93 vol-% compared to nitrogen's 78 vol-%, argon is much more energy intensive to produce[4]. The use of inert, noble gases has their specific uses, but should not be the default.

CONTINUOUS PROCESSING

Residence time

The scale-up of capacity from lab to test production, pilot production, and then commercial production often introduces new process limitations that were not observable at the previous scale: kinetic rate limitations due to temperature uniformity, peak temperature, and mass diffusion. These all can, if taken without optimization, lead to a significant residence time requirement in the heating chamber for the process. The volumetric rate times the residence time then leads to a larger furnace size with higher capital and installed utility costs, higher surface area for wall heat loss, and higher gas consumption. With operational consideration, this can even drive groups towards batch furnaces which are inherently inefficient, cycling the entire thermal mass of the heating chamber.

The residence time also helps frame in possible furnace types. At very short residence times less than 1 minute a dilute-phase vertical drop reactor may be suitable. With short residence times less than 2 hours a rotary tube furnace or dense-phase moving bed vertical reactor would be ideal. For longer residence times, the processes are usually limited to tunnel furnaces.

Non-optimized, long residence times may also have a negative impact for product quality of powder processing. Grain growth and agglomeration of particles can lengthen, or add entirely, a milling step downstream, which can be very energy intensive depending on the process material. The residence time requirement specified may be the single largest impact on energy efficiency on the thermal unit.

While not directly an energy efficiency issue, the amount of material held within the thermal process is proportional to the residence time. At start-up several of these volumes must pass through the process before steady state is established. At shut-down another volume of potentially off-spec material is produced. All or part of the value added by upstream operations can be wasted.

Ancillary Process Components

As mentioned above, sometimes the imposed long cycle times and material flow properties can quickly limit useable furnace types. The operation which heats only the process material and atmosphere as required will be lower than any other in terms of kWh/kg of product. With traditional heating methods, electrical resistance and hydrocarbon-fired, a furnace with no product carrier is optimal: rotary tube or vertical tube furnace for example. The material must be in powder, pellet or agglomerate format and be free flowing through the entire temperature range. Adding a carrier could double the energy input for sensible heats. Complex kiln furniture for stacking parts in a large furnace volume can range from 50-95+% of the load thermal mass.

In a batch furnace, the complex kiln furniture is typically required. This in addition to the entire thermal mass of the furnace shell, insulation, process containment, and process load is heated up and cooled down every cycle. This is in addition to the energy requirement that is seen on a continuous furnace when adding kiln furniture, described above. Now, the heating elements and connected load to the furnace are sized not for the energy going into the process, but the energy being thrown away heating and cooling the furnace itself. Energy and total operating costs are always higher with batch furnaces.

Atmosphere and Byproducts for Reuse

With a continuous furnace it is possible to configure the gas handling systems in complex, well integrated ways to recover heat. The key feature of a continuous furnace that enables the following solutions is an uninterrupted gas flow with steady gas composition. The steady gas flow and composition enables gas recycling, for example the recycling of hydrogen gas in a reduction process, or energy recovery, for example by oxidizing volatile organic compounds followed by a heat exchanger to preheat the furnace process atmosphere. In addition the system design can take advantage of the fact that in a continuous furnace all points in the process are occurring simultaneously but at different locations in the furnace. Consider a Pyrolysis process which evolves fuel-rich streams at the high-heat soak temperature of 750°C. The majority of the required heat input is in the preheating zones to bring the process material and atmosphere to 750°C. To take advantage, the fuel-rich exhaust can be externally piped and oxidized to provide heat to the preheating zones. However in a batch furnace the fuel is never around when it is needed, so the fuel-value of the process byproduct is wasted.

Wisely handling the incoming process atmosphere in a continuous furnace can also lead to energy benefits. The default way to manage the flow of the solid feed and gas feed in a thermal system is to introduce them counter-current to each other. And with good reason; the cold gas is preheated by the discharged product, and the hot product is cooled by convective heat transfer from the gas, often more efficient compared to conduction from water cooling. It is most effective when the summation of each material's mass rate times its heat capacity (effectively watts per Kelvin, W/K) in the opposing streams are matched, just like a well-designed heat exchanger. This arrangement is not possible in a batch furnace and no energy benefits will be gained.

MODELS AND EXAMPLES

Counter-current Gas Enhanced Heat Transfer Model

The following model was developed to expand on the above enhanced heat transfer concept of counter-current process gas. The model uses a rotary tube furnace 1 meter in diameter, 10 meters heated length, operated at 1150°C with 1000 kg/h of solids with a specific heat of 1000 J/kg-K. A coarse particle size of approximately 200 micrometers was considered. Particles of this size allow significant through flow of the process gas within the bed of material, enhancing gas-solid heat transfer. An overall gas to solid heat transfer coefficient of 50 W/m^2-K was considered. This would be expected to be significantly lower with a fine, not-free-flowing powder.

Figure 1 and 2 below illustrate the case of balanced and unbalanced mass rate times heat capacities for the opposing solid and gas streams. Figure 2 has twice the gas requirement of the balanced case. The temperatures of the furnace setpoint, solid and gas are plotted against the distance from the furnace entrance.

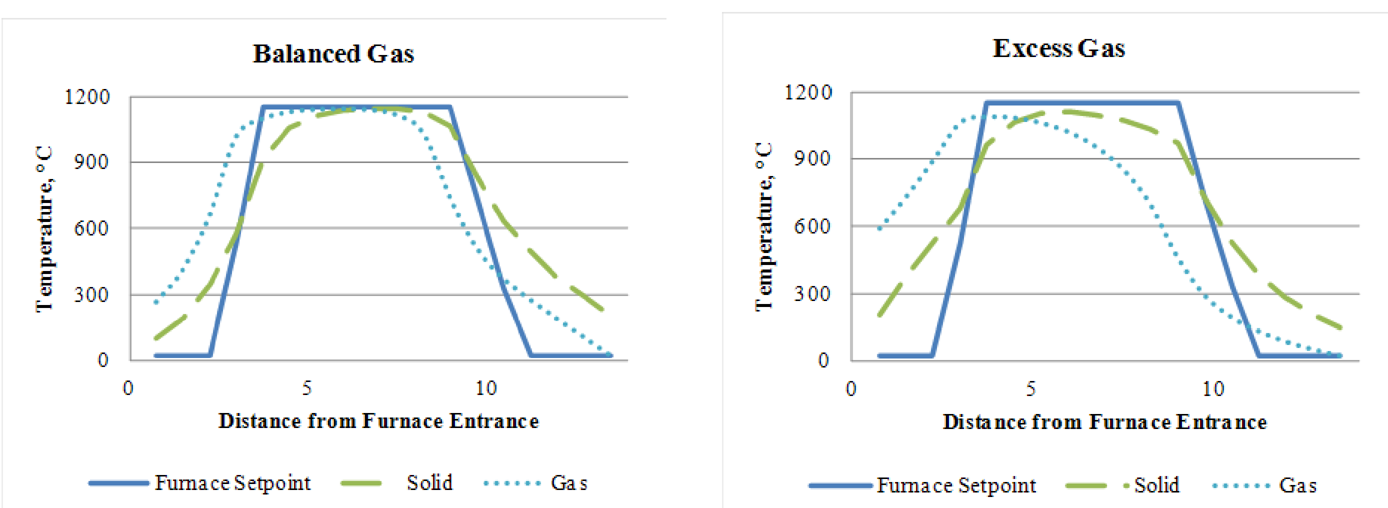

Figure 1 and 2. Plots illustrate the difficulty in controlling the temperature profile of the solid material in the furnace when the reaction is operated with significant excess mass rates of the gas.

A significant excess mass rate times heat capacity of the gas will enable faster cooling and preheating of the solid product. However, the energy required for the reaction is higher at 382 kW in Figure 2 compared to 170 kW in Figure 1. It also diminishes the temperature control of the solid material along the length of the furnace. The loss of temperature control is even more pronounced in situations where processes are developed with complex temperature profiles.

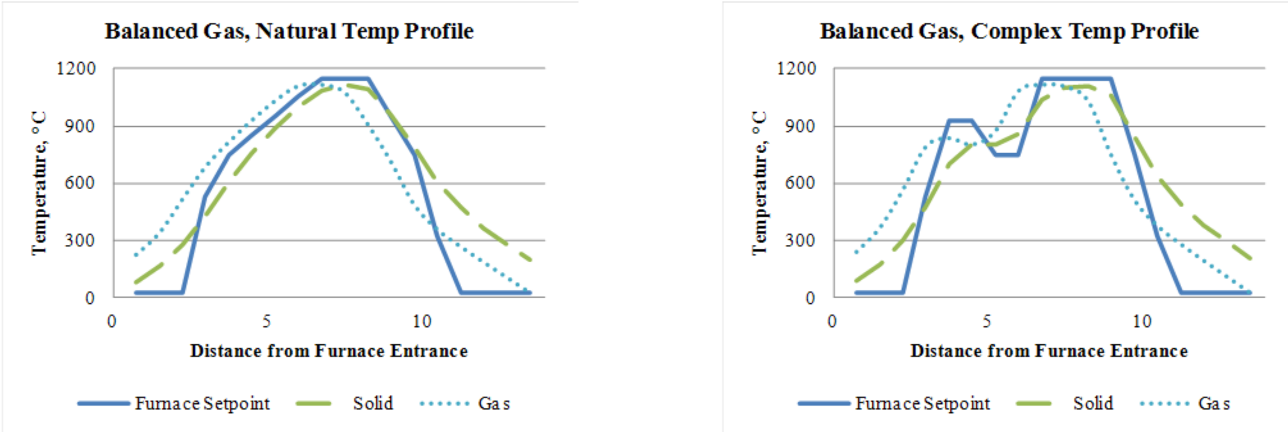

Figure 3 and 4. Plots illustrate the impact on solid and gas temperature profiles in the furnace with a natural temperature ramp rate and soak compared to an imposed complex temperature profile.

The counter-current strategy in Figure 3 works very well. The solid material is more closely held to the furnace setpoint. However, as seen in Figure 4, complex ramp rates with many zones of temperature control where you ramp, hold, ramp and hold may be ill-conceived with high counter-current gases. The sensible heat of the counter current gas will carry heat to the low temperature zones at the beginning of the furnace. Correcting the situation and lowering the counter-current gas rate will cause an unbalanced W/K in opposing streams. In addition, the scenario in Figure 4 requires approximately 10% more power at 156 kW compared to 142 kW in Figure 3. This sample model shows the benefits of a counter-current solid-gas heat exchange within a continuous furnace. While developing your process, consider the optimal process gas rates for both reaction kinetics and furnace heat exchange. In addition, be careful of scaling up complex time-temperature profiles from batch to continuous for the commercial production.

Metal Oxide Reduction Sample

For a small production operation of a particular metal oxide reduction, the reaction time and hydrogen gas requirements were so high that it was decided the process should be produced in a batch fluid bed furnace. In scale-up testing, alternative ways to reduce the oxide were investigated. Gas-solid interaction was critical so a rotary tube furnace with lifters was tested with similar gas flow rates. The material flowed uniformly off each lifter, mixing with the counter-current process atmosphere, but the residence time requirement pushed the limits of a rotary tube furnace at more than two hours. In addition, the quantity of reaction gas caused low yields due to significant powder entrainment in the gas stream. To improve, alternative reductants were investigated. Methane was chosen for its carbothermal reduction properties. Upon cracking it generates both carbon and two molecules of hydrogen.

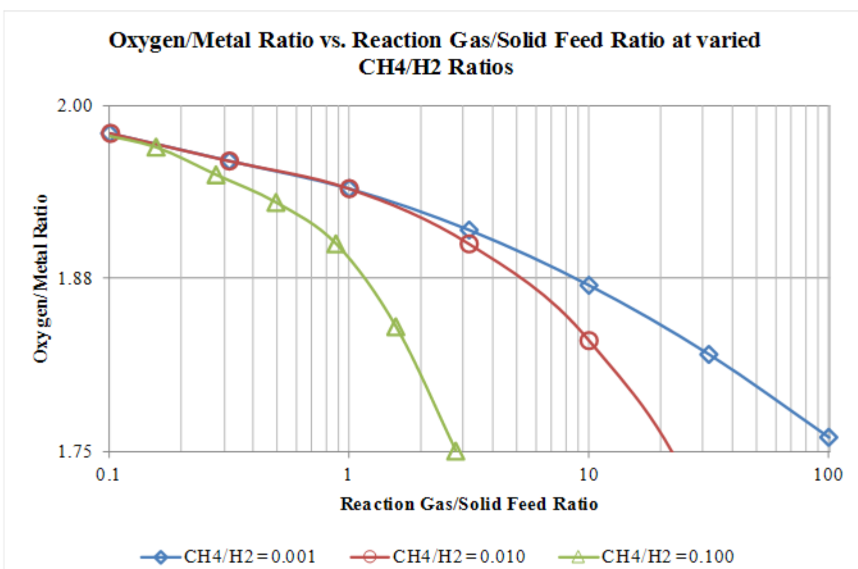

Figure 5. The target reaction completion was a reduction in the ratio of oxygen/metal atoms in the product from 2 to 1.75.

A small addition of methane improved the reaction time to have a uniform process and reduce the hydrogen consumption. Almost two orders of magnitude of gas quantity was saved by this addition. The gas utility cost and the energy to heat the gas to temperature could be significantly reduced. This discovery could allow the process to economically scale up to commercial production volumes.

CONCLUSION

The thermal process is a major consumer of energy in a commercial plant. The form of the commercial scale plant must be explored earlier in the development process. Even at the lab scale, where influences of gas quantities, temperature ramp rates, and materials of construction may not be critical, they should be considered with the end in mind. Optimizing the thermal process may also eliminate unit operations all together, such as powder milling and closed-loop water systems. Similarly, in consideration of furnace volume utilization it may be that an additional upstream step is required for eliminating low-temperature volatiles such as water in a dryer or high-temperature condensable solids in a wet-chemistry reactor. The benefits of a continuous furnace operation over a batch operation are increased up-time, product quality and consistency, decreased residence time, reduced power requirements, and integration for complex heat recovery or utilization from process byproducts. Every step of a new production scale will present a whole new set of factors that may not have been apparent. As you consider your process development, keep energy efficiency in mind.

REFERENCES

[1]C. K. Gupta and N. Krishnamurthy, *Extractive Metallurgy of Rare Earths,* Boca Raton, FL: CRC Press (2005), 61.
[2]V. Immanuel and K. Shee Meenakshi, Synthesis of Carbon Cloth by Controlled Pyrolysis of Rayon Cloth for Aerospace and Advanced Engineering Applications, *Indian J. Science and Technology*, 4(7), 759 (2011).
[3]S. Sriramulu et al., Implantation, Activation, Characterization and Prevention/Mitigation of Internal Short Circuits in Lithium-Ion Cells, 2012 DOE Annual Merit Review Meeting, 14-18 May 2012.
[4]F. R. Field, J. A. Isaacs and J. P. Clark, Life-cycle Analysis of Automobiles: A Critical Review of Methodologies, *J. Minerals, Metals and Materials Soc.*, 46(4), 12-16 (1994).