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Operating Flexibility in the ReACT™ Multipollutant Control System

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ReACT™ (Regenerative Activated Coke Technology) is an advanced multipollutant control process which has been successfully applied in Japan over the past fifteen years on coal fired boilers up to 600MW and on major sinter plant operations in the steel industry. For the U.S., ReACT™ has been included in an EPA listing of "innovative and emerging technologies" which "offer the potential of reduced compliance costs and improved environmental performance" and can be considered candidates for commercial demonstration permitting under the national NESHAP standards for electric generating utilities proposed under section 112 of the CAA.

Hamon Research-Cottrell offers the ReACT™ process to U.S. utilities under license from J-Power EnTech.

Japan's largest operator of coal fired power plants, J-Power, acquired technology rights to the process from Mitsui. J-Power now operates ReACT™ at three coal fired units: Takehara (1995), Isogo #1 (2002) and Isogo #2 (2009) and is developing plans for ReACT™ at the upcoming repowering of Takehara.

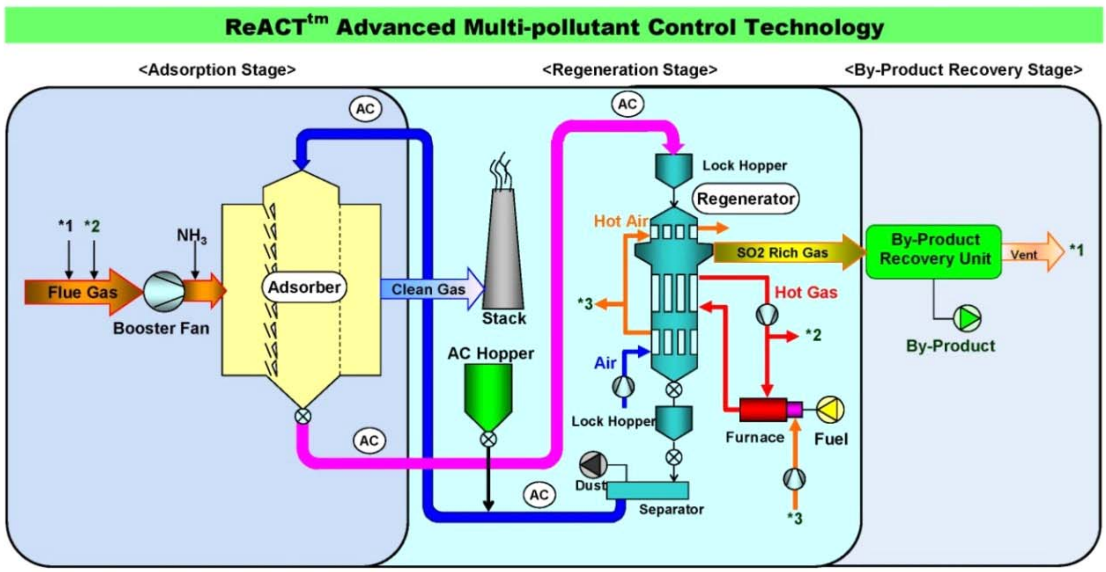
J-Power's Isogo facility ranks among the cleanest coal fired power plants in the world with SOx and NOx emissions routinely in single digit ppm concentration.

The process provides high efficiency capture of SO_2 and SO_3 by ammonia promoted surface adsorption in a cross-flow moving bed of activated coke. ReACT™ also provides co-benefit NOx control, particulate reduction, dioxin/furan control and high capture of elemental and oxidized forms of mercury. Higher NOx control levels can also be achieved through adsorber and regeneration design and operation.

The design and operation of the process allows flexibility for optimization of compliance, operation cost, and maintenance planning. This paper reviews aspects of the ReACT™ process and operations during start-up, shutdown and maintenance.

<u>ReACT™ process</u>

ReACT™ is a three stage dry process which does not use water and minimizes the production of disposal wastes. The process provides for control of SO_2, SO_3, acid gases, particulate, Hg, and NOx.



1. <u>Adsorption in the presence of ammonia across a moving bed of activated coke</u>

    a. SO_2 and SO_3 are Hg are removed at very high efficiency (SO_2: 95-98%+, SO_3: 98%+)
    b. Hg is removed at very high efficiency (95%+)
    c. AC surface is provided for the low temperature catalytic reduction of NOx. (20% to 60% with secondary NH_3 in the regenerator)
    d. A net reduction of particulate emissions is a result of impaction and interception mechanisms. (~50% reduction)
    e. Clean flue gases at normal flue gas temperature are sent to the stack
    f. Carbon steel construction

2. <u>Thermal regeneration of the activated coke</u>

    a. Removes the adsorbed species and allows reuse of the activated coke.
    b. Retains mercury compounds in the regenerator for periodic disposal
    c. Produces a concentrated sulfur rich gas stream

3. <u>By-product production</u>

    a. Sulfur rich gases are processed to marketable sulfuric acid.

In ReACT™, activated coke in pellet form is continuously cycled between adsorption and regeneration.

Adsorption

Designed to meet project-specific requirements, a ReACT™ adsorber vessel is comprised of a number of moving beds that operate in parallel. Each bed is a single pass device, which is top fed with regenerated activated coke. The AC flows by gravity at a rate controlled by a roll feeder at the bed discharge.

The moving bed provides highly efficient contact between the activated coke and the incoming flue gas to which ammonia has been added. Flue gas flows at low velocity across activated coke pellets with a very large surface area of high capacity adsorbent for control of SO_2 and acid gases.

Gas space velocity in the range of 350-450 hr-1 and activated coke residence times of 80-120 hours are typical. These contacting conditions in the adsorber provide approximately 10 seconds for the flue gas to transit the activated coke bed and the activated coke moves very slowly in the bed.

Compared to powdered activated carbon in a fabric filter, for each unit of flue gas, the moving bed provides a significantly longer time-surface interaction and two orders of magnitude more carbon surface for adsorption. This results in highly efficient control for both elemental and oxidized forms of Hg as a co-benefit of the process.

The activated carbon surface also provides for co-benefit reduction of NOx via both catalytic and non-catalytic mechanisms that are enhanced by the presence of ammonia. A minimum co-benefit of 20% NOx control is typical. If NOx control in the range of 40-60% or above is desired, the NOx activity of the activated coke can be increased with the injection of ammonia in the regenerator.

All NOx control reactions in the adsorber are the reduction of NOx compounds to N_2. These reactions do not create adsorbed species on the activated coke.

The process operates at flue gas temperatures without humidification of the flue gas. Since the adsorption process provides near complete removal of SO_3 with no flue gas humidification, there is no increase in water plume and negligible potential for acid plume. The adsorber gas path is carbon steel and the cleaned exhaust gases can flow directly to an existing stack, with no need for stack liner upgrades.

Regeneration

Activated coke from the moving beds is mechanically transported to the regeneration stage.

Adsorbed species on the activated coke surface include sulfuric acid, water, ammonium sulfate and ammonium bisulfate. These species are removed by thermal regeneration. Adsorbed mercury compounds are desorbed and readsorbed in the regenerator and remain in the regenerator due to its counter flow operation. As noted above, NOx removal in the adsorber ($NO/NO_2 \rightarrow N_2$) does not add adsorbed species for regeneration.

Each regenerator is top fed with activated coke through nitrogen purged lock hoppers. The AC pellets flow by gravity on the tube side of the indirect heat exchanger section. Nitrogen is introduced at the base of the regenerator as a carrier gas that sweeps the desorbed gases upward while the AC flows downward. The AC pellets leave the regenerator through a nitrogen purged lock hopper to a roll feeder which controls the AC throughput rate.

The regenerator vessel is a vertical three stage indirect heat exchanger, with a AC feed section at the top, followed by an upper preheat section, an upper isothermal zone from which the sulfur rich gases are extracted, a heating section , a lower isothermal zone to promote complete desorption, and a lower cooling section and discharge section.

Kinetics for SO_2 desorption from activated coke was described for the earlier Bergbau Forschung process as shown in the following figure excerpted from Reference 1.

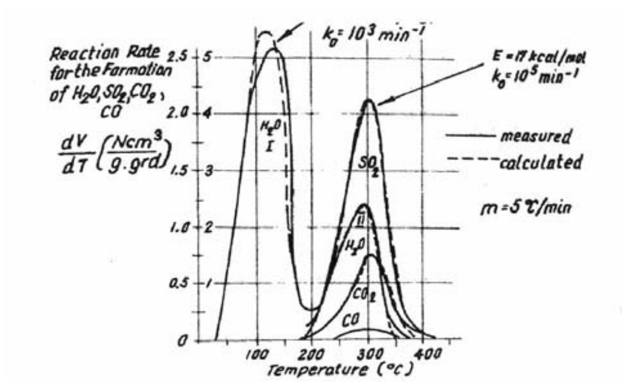
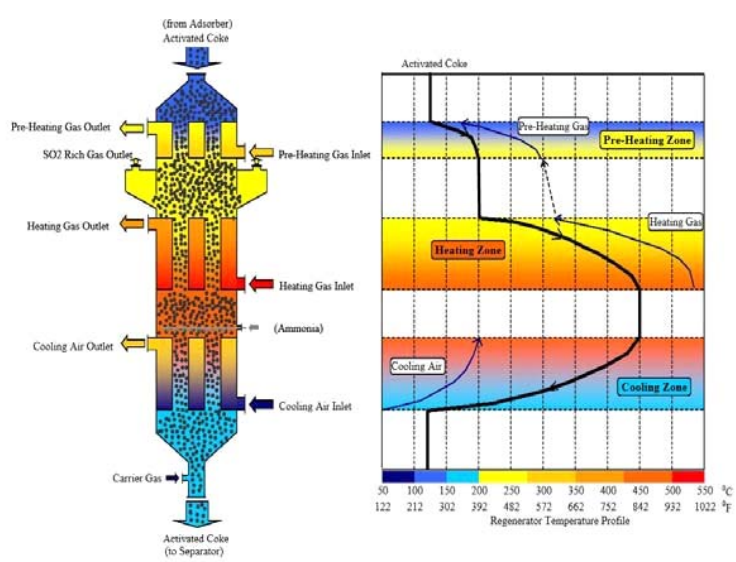


Figure 2. Nonisothermal kinetics of thermal regeneration

The regenerator operation and temperature profile directly follows the kinetics set forth above.



Activated coke is fed to the tube side of the preheat section where the activated coke temperature is increased to 200C. Free moisture is released at 100C. As temperatures approach 200C, gases related to the adsorbed sulfur compounds begin to be released.

The reactions occurring in the regenerator include the decomposition and release of the adsorbed sulfur and ammonia species as a sulfur rich gas primarily composed of SO_2, H_2O, CO_2 and N_2.

$$H_2SO_4^* + 1/2\ C \rightarrow SO_2 + 1/2\ CO_2 + H_2O$$

$$(NH_4)_2SO_4^* \rightarrow SO_3 + NH_3 + 2\ H_2O$$

$$NH_4HSO_4^* \rightarrow SO_3 + 2\ NH_3 + H_2O$$

$$3\ SO_3 + 2\ NH_3 \rightarrow 3\ SO_2 + 3\ H_2O + N_2$$

The heating section brings the activated coke from 200C to 450C. Peak desorption rates are reached near 300C in the middle of the heater tube sections. By the time the activated coke temperature reaches 450C the rate of desorption is slowed and approaching zero. An isothermal zone at 450C promotes complete desorption of the sulfur and mercury vapors which are swept upward by nitrogen carrier gas flowing from the cooling section below.

The cooling section brings the activated coke temperature back to the flue gas temperature or below, making the coke ready for fines separation and return to the adsorber beds.

A unique aspect of ReACT™ counter flow regeneration is the re-adsorption and retention of mercury vapors at the top of the heating section, where 200C down-flowing coke meets up-flowing Hg gases which had been released at 450C. The re-adsorbed mercury accumulates in this specific temperature zone of the regenerator. The activated coke in this zone has sufficient capacity to retain the mercury for two or three years before breakthrough. This enables the periodic scheduled disposal of mercury laden material. Since the mercury laden AC waste is less than 0.1 tons per MW per year, this represents a significant waste volume minimization compared to other mercury options.

Process stability and turndown - Key process parameters

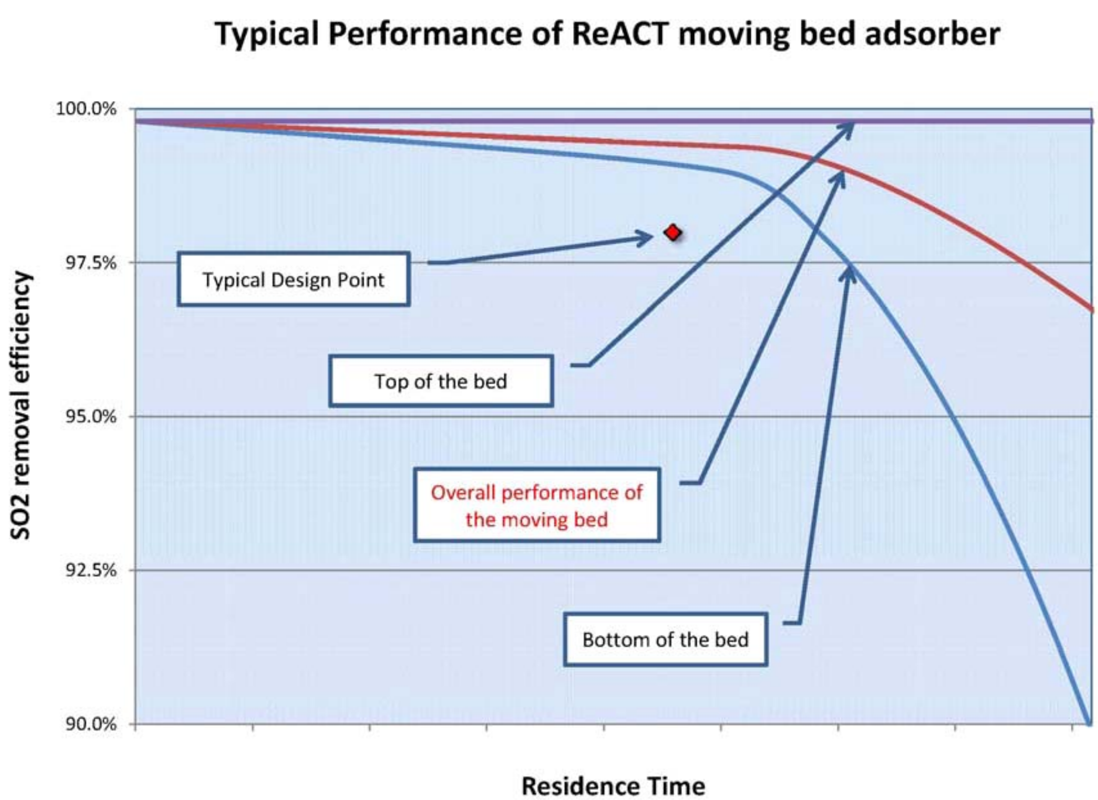
The ReACT™ system is designed based on the maximum volumetric flow, temperature, SO2 and NOx loading conditions specified for a given project. These worst case conditions are evaluated to determine a design solution for the activated coke adsorber beds and the activated coke throughput rate. All other operating conditions represent a lower duty compared to the design case and turndown in a cycling boiler is easily handled.

Some process parameters which influence ReACT™ SO2 performance include:

- Flue gas space velocity is the volumetric flow divided by the volume of the activated coke bed. At lower boiler load, the space velocity is reduced, the flue gas has longer time in contact with the activated coke and the adsorption efficiency for SO_2 is improved. Similarly, the carbon surface contact time as catalyst for NOx reduction is extended.
- Similarly the circulation rate of the activated coke through the moving bed volume determines the activated coke residence time. This time period between introduction of activated coke at the top of the adsorber bed and discharge of activated coke (plus adsorbed species) at the bottom of the bed is typically 80-120 hours at full load.
  - At full load with the highest inlet SO_2 condition, design residence time determines a maximum activated coke circulation rate.
  - For typical operation, if the maximum circulation rate is maintained, the system will operate at higher SO_2 efficiency.
  - If the system is controlled to maintain SO_2 compliance, the circulation rate bed speed can be reduced for typical operation.
  - The activated coke residence time in the adsorber is typically several days. Since this residence time is multiples of the typical boiler load cycle, any flue gas process fluctuations due to load cycling or coal feed are averaged out in the beds. The downstream regenerator gets a stable feed condition which reduces turndown and sulfur rich gas variance at the acid plant.
- The system is designed at a maximum flue gas temperature based on full load conditions. The performance of adsorption process improves with lower temperature, so reduced temperatures from turndown or seasonal variation will improve SO_2 efficiency.
- Higher SO_2 efficiency is also favored at lower inlet SO_2 concentration since the design of the moving bed is such that the SO_2 capacity of the bed is not reached at the maximum SO_2 load condition.
- SO_2 adsorption is only slightly affected by variation in flue gas oxygen and moisture levels. Typical variations in flue gas oxygen and moisture offset each other with respect to SO_2 adsorption.

Operating simplicity and stability – moving bed performance

For any individual activated coke pellet, adsorption by combined physical adsorption and chemisorptions starts and continues at very high rates until the adsorbed species has filled the carbon matrix to monolayer saturation. Beyond this point, adsorption continues but at reduced rates and performance eventually falls off to 90% efficiency or "breakthrough" levels. The design point for any project is determined to avoid approaching breakthrough levels at the bottom of the bed and includes additional operating margin.



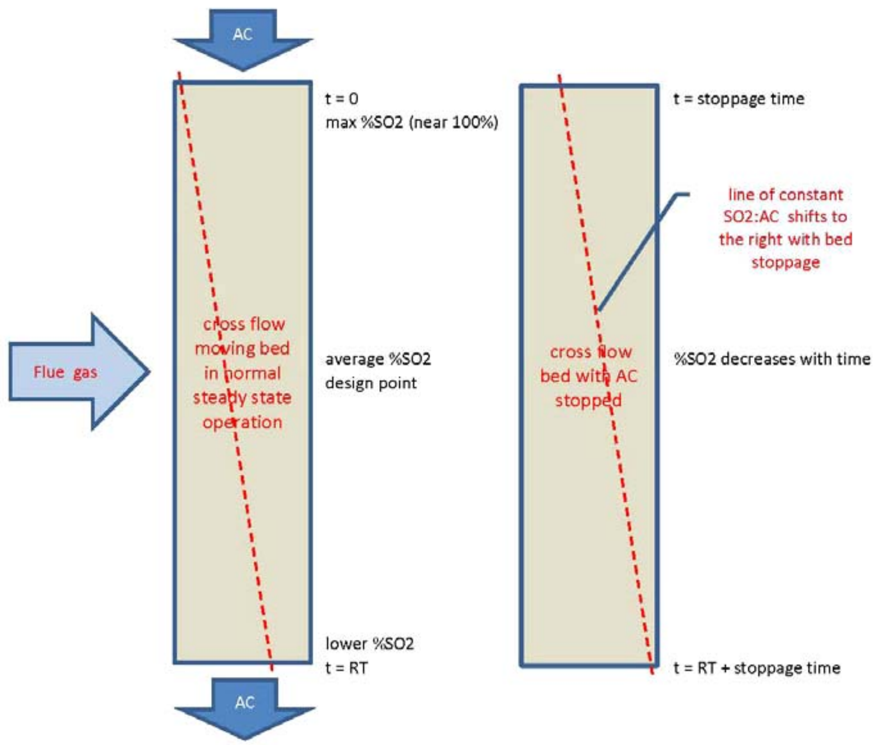
The design point for the ReACT™ system is in the high adsorption rate region.

In the moving bed the activated coke the top of the bed is continually replenished with fresh material. The performance at the top of the bed is always near 100%.

The local performance at the bottom of the bed is analogous to an individual activated coke pellet as a function of exposure time. Adsorption efficiency at the bottom of the bed is lower as more of the sorption capacity is used.

The overall performance of the moving bed is shown above as a function of residence time and represents the cumulative time average performance of all of the activated coke in the bed.

The SO_2 performance of a moving bed is also illustrated in the following graphic which represents a simplified moving bed and a stopped bed. If activated coke circulation is stopped, high level performance continues for some time, falling off gradually as the sorption capacity of the bed is used.



For this example, consider that in normal operation of a bed with activated coke circulation rate adjusted to operate at the design point. SOx efficiency will be at/above the target efficiency. Activated coke feed accumulates SOx over a nominal residence time of about 100 hours as it moves to the bottom of the bed.

For a long-term steady-state operation, performance can be approximated by considering a line representing constant adsorbed SOx:AC load. The efficiency at various distances down the bed can be thought of as being related to this line. At the top of the bed the activated coke has minimal exposure to flue gas and the capacity of the activated coke to adsorb SO_2 is at its maximum. The SOx efficiency at the top of the bed approaches 100%. At the midpoint of the bed, the SOx efficiency is near the average performance of the bed (i.e. near the design efficiency). With a straight line representation, if the design efficiency for SO_2 is 97.5% at the midpoint of the bed, the efficiency at the bottom of the bed efficiency at the bottom of the bed is about 95%.

Providing a 24 hour "grace period" for maintenance while maintaining full compliance can be reasonably assured in any operating scenario and can be further assured by operating at slight over-compliance using the AC circulation capacity to advantage.

Considering that a typical ReACT™ system for a large utility boiler will have multiple (20 or more) moving beds operating in parallel, stoppage in any individual bed, can be allowed for routine maintenance activities with little impact. In this example, stoppage for an entire system might see a decline in SO2 reduction efficiency of about 1% per day.

The actual grace period depends on the operating duty over the previous period and is increased with prior operation at higher circulation rates (lower residence time), or by any prior boiler low load operation.

Some Operations and Maintenance Scenarios

- Boiler start-up: Boiler flue gas flow can be permitted to pass through the activated coke beds from the initial fan start-up. Since low temperature is favorable for SO_2 performance compliance is immediate.

- In the event of a fuel trip, compliant operations can be maintained during the trip as flue gas flow continues through the system.

- In the event of a station loss of power and master fuel trip, the flue gas path through the adsorbers remains open and compliant stack conditions can still be met. Flow through the system would be limited by stack draft. In the regenerator area, the process heater would trip, activated coke flow would stop and the rate gas desorption would quickly drop. SRG flow to the acid plant would stop.

- Normal scheduled shutdown for outage ---- with boiler load rollback and decrease/stop of fuel, flue gas which is now decreasing in flow rate, temperature and SO_2/NOx loading continues to flow through the adsorbers. Regeneration operations can continue and SRG can flow to the acid plant for processing. Depending on the anticipated length of the outage, systems can be bottled up to preserve heat and or shut down. Longer term outage shutdowns would involve proscribed procedures for equipment shutdown, cooling and purge which anticipate maintenance or inspection activity.

- Material handling stoppage (any conveyor or device) ---- stoppage of material handling would interrupt normal operation of either/both the adsorber casings or regenerators initiate alarms and require corrective action. The grace period in the ReACT™ adsorber system provides for predictive maintenance and inspection. Each cartridge has a roll feeder discharge. Since all adsorber bed cartridges operate in parallel, stoppage at an individual roll feeder has minimal effects on overall performance.

- Regenerator stoppage --- trips at the regenerator equipment (fans, heaters, material handling) would stop operations at the regenerator and reduce the amount of SRG flow to the acid plant. Coke speed through an operating regenerator may be increased temporarily.

Summary

The design for ReACT™ considers the key process parameters discussed above as well as a "grace period" to allow for maintenance of upstream and downstream material handling. The overall process is inherently stable with good turndown capability.

During operation, one or more of the design basis criteria are usually below their maximum rate, and the duty for the ReACT™ system can be satisfied with a reduced activated coke circulation rate. However, the capability to run at higher activated coke circulation provides operating flexibility for the system, in the form of extended margin for environmental compliance and/or planning for maintenance activities.

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