Mercury Control with Regenerative Activated Coke Technology

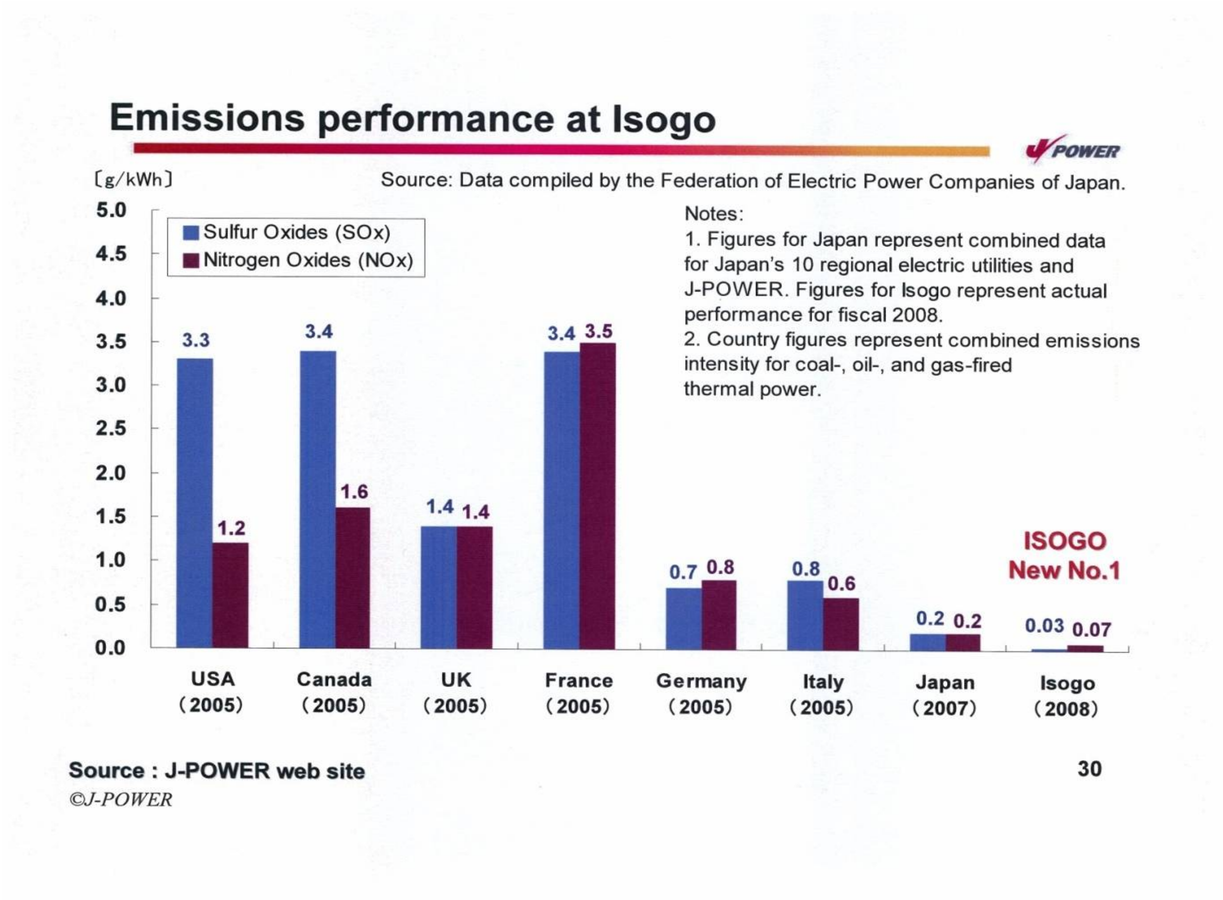
H. James Peters,
Executive VP Products/Technology
Hamon Research-Cottrell, Inc., Somerville, NJ
james.peters@hamonusa.com

Background

The multi-pollutant control ReACT™ technology is a completely dry scrubbing system based on adsorption of SO2, SO3, and Hg and reduction of NO_x to N_2 on activated coke in a moving bed, with regeneration of the coke for return to the adsorber, and production of saleable byproduct, such as sulfuric acid, from desorbed sulfur rich gases.

The basic process concept originated with Bergbau Forschung in Germany the 1950s, saw additional development by Foster Wheeler in the 1970s in conjunction with their Resox process, and commercialization with activated coke by Mitsui Mining in the 1980s, and subsequent full commercialization by EPDC (now J-Power) in the 1990s as an advanced generation multipollutant control technology for coal fired boilers. J-Power, acquired the technology from Mitsui in 2005, now operates three full scale units at Takehara (1995), Isogo #1(2002) and Isogo #2 (2009), and has provided units for refinery, incineration, and sinter applications through its subsidiary J-Power EnTech.

J-Power's Isogo #1 and Isogo#2 burn low-sulfur coal and incorporate high efficiency ultrasupercritical boilers, combustion NO_x control, primary SCR, ESPs and ReACT™. Isogo has been recognized for emissions intensity levels for SO_x and NO_x that are the lowest worldwide for coal fired power. Isogo typically operates in the single digit ppm concentration range for SO_2 and NO_x (against permit levels of 10ppm and 13 ppm at Isogo #2), particulate at less than 5 mg/Nm3 (0.005 lb/mmBTU) and with well over 90% control of both elemental and oxidized forms of mercury.



Emissions performance at Isogo

Source: Data compiled by the Federation of Electric Power Companies of Japan.

Notes:
1. Figures for Japan represent combined data for Japan's 10 regional electric utilities and J-POWER. Figures for Isogo represent actual performance for fiscal 2008.
2. Country figures represent combined emissions intensity for coal-, oil-, and gas-fired thermal power.

Source : J-POWER web site

30

©J-POWER

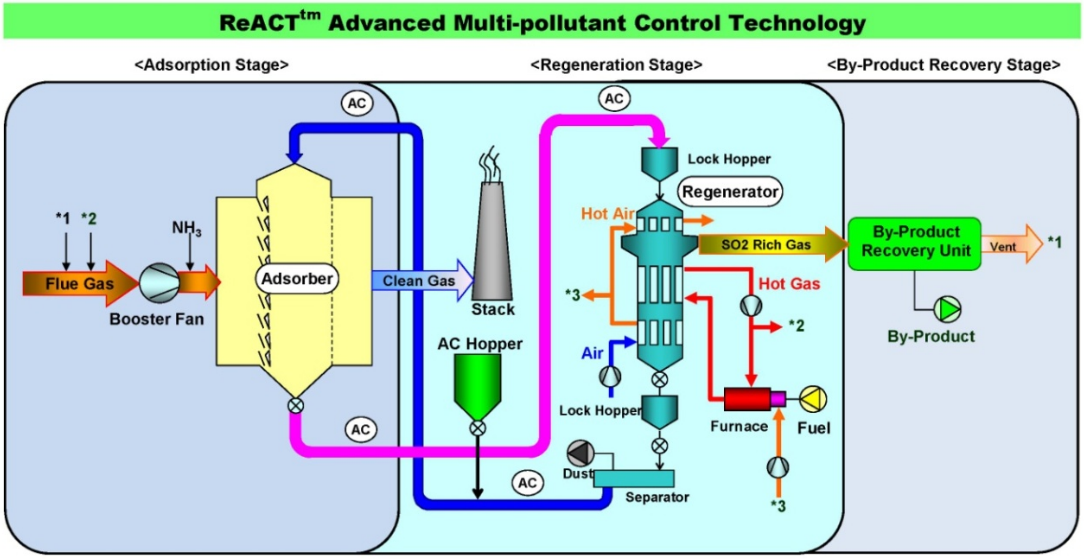
The ReACT™ process has also been already been successfully demonstrated for U.S. coal applications as an EPRI project, hosted by Sierra Pacific Power at its North Valmy Station, where the expected high levels of SO_2, NO_x, and Hg performance were readily demonstrated, consistent with commercial results at the full scale units in Japan.

This paper focuses on aspects of the activated coke technology as related to mercury control.

General process description

ReACT™ involves a three stage process. Flue gas is contacted with a slowly moving bed of activated coke. Fresh activated coke is fed to the top of an adsorption column and flows by gravity. The activated coke removes SO_2, SO_3, NO_x, Hg and other species through adsorption, chemisorption and catalytic reactions which are enhanced in the presence of ammonia. Particulate is also reduced across the moving bed by impaction on the coke pellets.

Pollutant laden activated coke is transferred to a thermal regeneration stage, where reactions are completed and pollutants are desorbed as a sulfur rich gas stream. The regenerated activated coke stream is cooled and fines are separated before return to the adsorber. Make-up coke in pellet form is added to replace the separated fines. The third stage receives the sulfur rich gas stream for saleable byproduct production.



This process offers advantages for utilities, as requirements for mercury control are being added to increasingly stringent SO_2 and NO_x regulation, and where issues related to water use, downstream plume visibility, and solid waste disposal have become major factors. These advantages derive from:

- Adsorption does not require any water use
- Adsorption of SO_3 along with no humidification resolves downstream plume visibility issues
- Regeneration of sorbent greatly reduces site logistics for reagent make-up, processing and waste handling compared with other FGD processes
- Marketable byproduct is produced.
- Primary particulate is upstream (existing), preserving beneficial use of ash.
- Mercury control is obtained at >90% levels for both elemental and oxidized forms.
- Mercury laden disposal streams are minimized.

Mercury control by activated carbon

The present practice for mercury control at utility power plants typically involves the injection of powdered activated carbon into flue gas.

Activated carbon is injected into the flue gas stream upstream of particulate collection equipment as a once-through adsorbent. For target mercury removal of 90% activated carbon injection rates range from 2 to 10 lb per million acfm with some sensitivity to coal, combustion, SO_3 levels and on the type of particulate control in place. Injection rates are generally lower with fabric filters.

Contacting conditions for activated carbon in a fabric filter include short in-flight time (1-2 seconds) followed by fixed bed contact at the fabric surface of less than 0.2 seconds with average solids residence time on the fabric surface of about 4 hours. The high specific surface area of powdered activated carbon allows control of mercury at 90% levels

Mercury reduction by adsorption on activated carbon occurs co-currently with particulate removal by the ESP or FF. The result is that the mercury laden carbon is mixed with the flyash and impairs the beneficial use of flyash such as for use in cement.

Activated coke vs. activated carbon

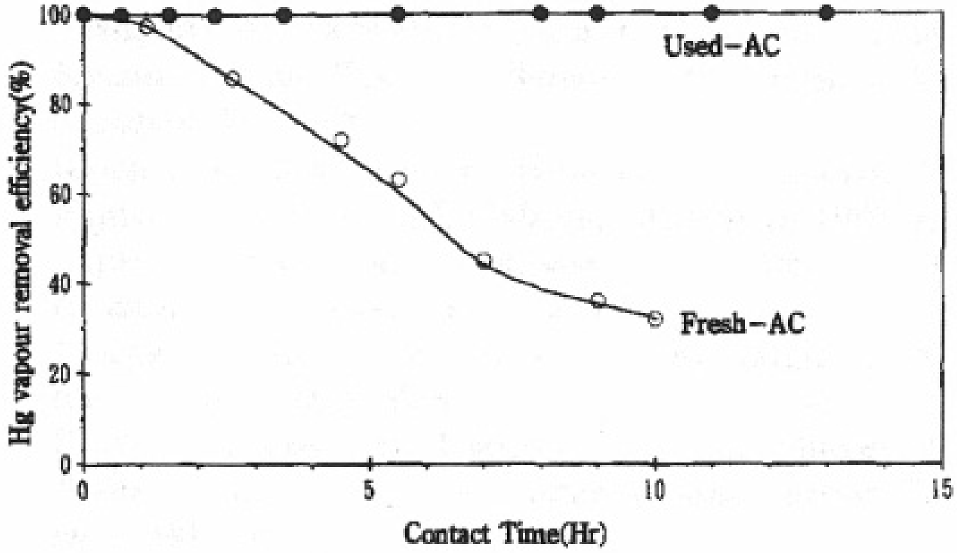
The ReACT™ process uses activated coke in pellet form suitable for use in the moving bed adsorber. This material generally compares with powdered activated carbon as follows:

	Activated Coke	**Activated Carbon**
Shape/Diameter	Tablet/Almond ~10 mm	Powdered
Specific Surface Area	150-300 m^2/g	>1000 m^2/g
SO_2 adsorption capacity	60-120 mg/g	
Pore size	10-1000 A	10-100 A
Pore volume	0.05-0.1 cc/g	0.5-0.6 cc/g
Roga-Index (abrasion resistance)	95%	70-85% (for tablet forms)
Raw Material	Coal	Coal
Application	SO_x, NO_x, Hg removal	Hg removal

Mercury control by activated coke

The ReACT™ adsorber design is determined based on SO_2 control requirements and gas space velocity of 400 hr^{-1} and activated coke residence time of 80 hr are typical. Contacting conditions in the adsorber are approximately 10 seconds for the flue gas to transit the moving activated coke bed. Coke pellets are exposed to flue gas for 80 hours.

Regenerated (used) activated coke also has found to have superior performance compared to fresh make-up material. During the regeneration process, new carbon pores are exposed during SO_x desorption by reactions which consume some carbon, and some sorption sites become functionally enhanced by the formation of oxygen species or by trace sulfur compounds. The following figure excerpted from Reference 2 shows results of bench tests at Mitsui where near 100% control of elemental Hg persisted for used AC at longer solid contact times whereas breakthrough occurred earlier for fresh material. Similar improved characteristics for SO_x and NO_x control are seen with used AC.

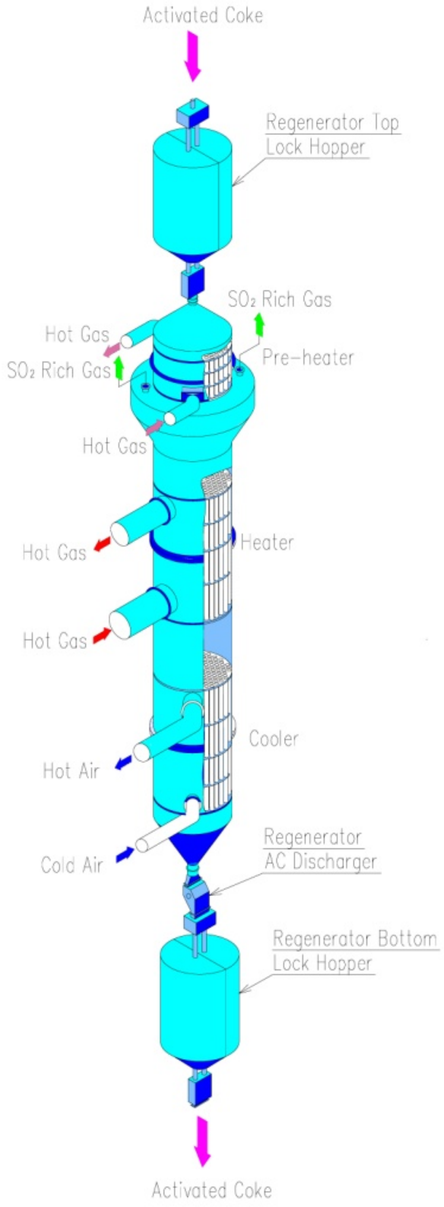


Hg(0) vapour removal test with AC (fresh versus used)

While fresh activated coke has lower specific surface area the contact time in the adsorber bed is significantly longer and the regenerated activated coke is present in considerable excess relative to mercury. This configuration results in highly efficient mercury reduction and Hg control for both elemental and oxidized forms in excess of 90% is readily achieved.

<u>ReACT™ Activated Coke Regeneration</u>

Following is a schematic of a typical ReACT™ regenerator which thermally desorbs sulfur rich gases.



Activated coke at flue gas temperatures carrying adsorbed SO_2, NO_x and Hg is fed through a lock hopper to the top of the regenerator   Activated coke moves downward by gravity flow through three indirect heat exchanger sections for preheating, heating, and cooling the regenerated coke which is then discharged through a lock hopper to fines separation and then returned to the adsorber.

A sulfur rich gas zone is located between the preheat and heating sections of the regenerator tower. The sulfur rich gas released (SO_2, N_2, CO_2, and H_2O) in this zone then flows to an acid plant for production of marketable sulfuric acid.

Prior to cooling the activated coke, ammonia gas can be sparged into the regenerator to pre-condition the activated coke for optimal SO_2 and NO_x sorption and the activated coke is cooled back to the flue gas temperature or slightly below.

The design of the heat exchanger control of the shell side heating and cooling air temperatures and flows provide the required temperature and residence time profile to complete the regeneration.

The nonisothermal kinetics related to thermal regeneration were illustrated for the Bergbau Forschung process in the following figure excerpted from Reference 1. The kinetics show that the thermal desorption can be driven to completion by heating the activated coke to 450C.

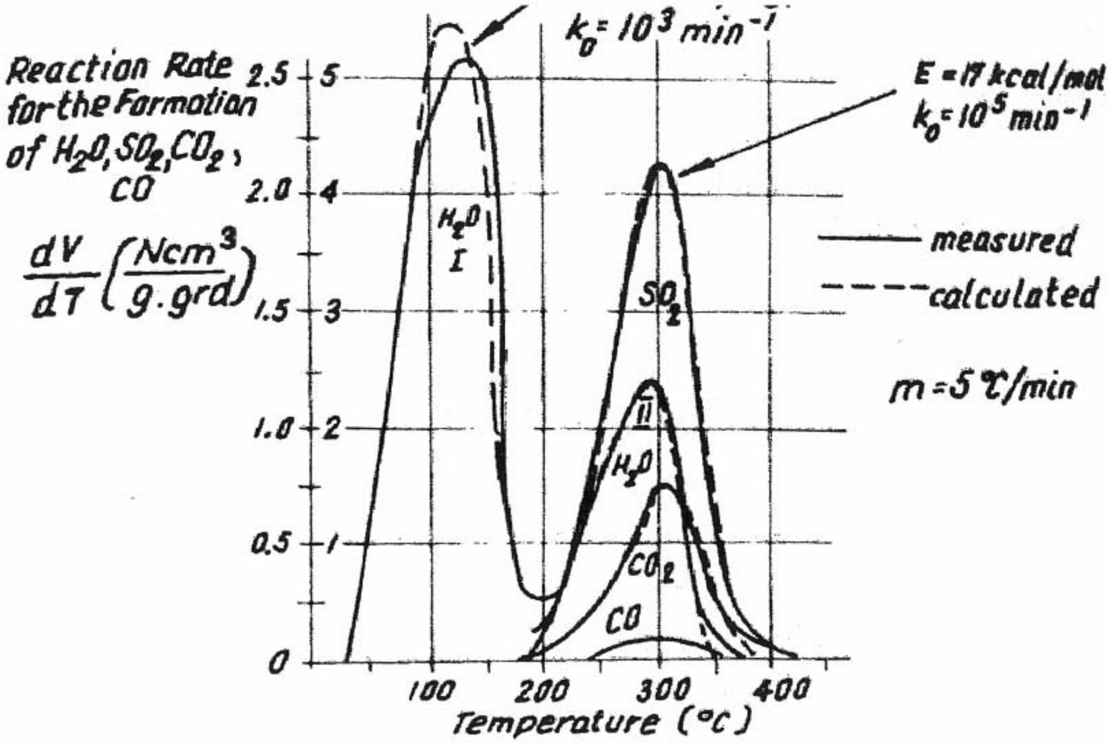
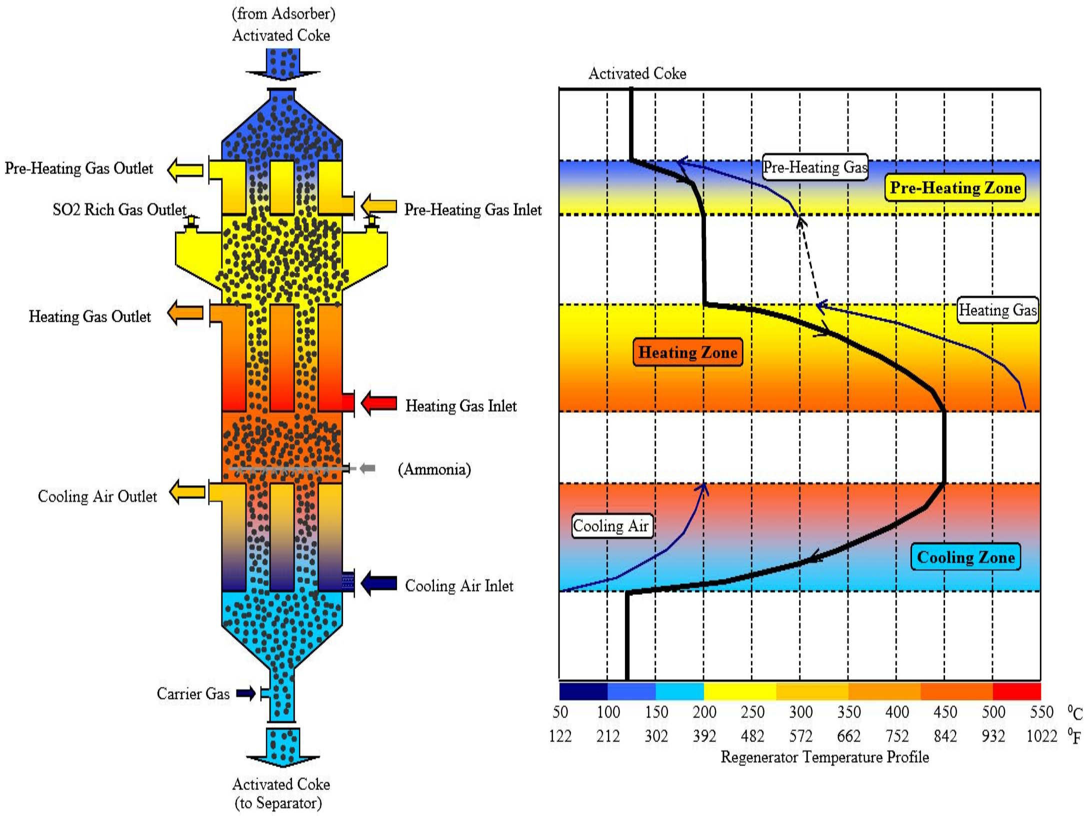


Figure 2. *Nonisothermal kinetics of thermal regeneration*

Mercury retention in the regenerator

In the ReACT™ regenerator temperature profiles and retention time at 450C allows the regeneration process to approach completion in accordance with the kinetic requirements.

Mercury vapors are also desorbed but mercury is held in temperature regime determined by the adsorption and thermal desorption properties of the activated coke. The longer term retention of mercury allows for improved management of mercury laden materials as only periodic disposal of activated coke from the mercury confined zone is needed.



Mercury is thermally desorbed at >400C to the vapor phase. The temperature profile of the regenerator shows that this temperature is reached within the heating zone. Mercury desorption is complete at the bottom of the heating zone at 450C.

Mercury and other desorbed gases flow upward and counter-current to the activated coke flow and contact lower temperature coke surfaces. At the top of the heating zone, the activated coke at 200C has effectively re-adsorbed all the mercury vapors.

The mercury that had been originally removed from the flue gas in the adsorber vessel is effectively confined in this zone of the regenerator.

Logistics for carbon make up and disposal

Over time the mercury accumulation in this zone approaches a saturation capacity. Depending on the level of mercury in the coal this period is typically in the two to four year range. At Isogo, three years is used as a planning interval and at each of the 600 MW plants approximately 100 tons of mercury laden activated coke are disposed every three years – or approximately 0.06 tons/MW-year.

Disposal is managed during a scheduled regenerator downtime (all activated coke has been cooled) by diverting the portion of activated coke that had been in the heating zone and lower SRG zone.

A comparison of the carbon make-up and disposal requirements for a typical 200 MW plant using once-through activated carbon compared to regenerative activated coke illustrates a significant difference is the issues related to Hg-laden material disposal.

Basis: 200 MW PC boiler burning low-sulfur PRB, 75% capacity factor

Firing rate: 2200 MMBTU/hr (at 11,000 BTU/kWh)

Flue gas flow: ~800,000 acfm @ 300F

Flyash load: 2 to 3 gr/acf (45,000 tons/year @ 2 gr/acf)

Hg load: 5 to 10 lb/10^{12} TBTU

For the ReACT™ process, fresh make up activated coke replaces losses due to fines separation after regeneration and carbon consumed in regenerator reactions. Make-up for a 200MW plant is approximately 1000 tons/year (4 to 6 tons/year per MW). This mercury-free material is either disposed of, used as fuel, or may have beneficial re-use as a carbon sorbent at other sites.

For a regenerator serving a typical 200 MW coal fired boiler, this would be about 20 to 25 tons of activated coke, and if the disposal interval is two years, the disposal rate would be roughly 12 tons/year or (0.06 tons/MW-year).

For typical activated carbon systems, 90% mercury control requires injection of powdered activated carbon (PAC) into the flue gas at rates between 2 lb/MMacfm and 10 lb/MMacfm. The higher rates are generally associated with injection is upstream of an electrostatic precipitator, and lower rates with injection upstream of a fabric filter. Injection rates have some sensitivity to fuel type, boiler type and effects of increased SO_3 from upstream SCR.

When the powdered activated carbon is injected upstream of the primary particulate control, whether it be an ESP or a fabric filter, the flyash is then contaminated with mercury laden carbon which may render otherwise saleable flyash for cement or road material into landfill waste. If activated carbon is injected into a secondary fabric filter placed downstream of an ESP (which may be powered back to control the PAC/ash mixture at the FF to about 10% carbon, activated carbon usage can be minimized and flyash beneficial use maintained but with additional equipment and energy requirements.

Basis	200 MW, 800,000 acfm @ 300F, 75% capacity factor, >90% Hg control			
	Powdered Activated Carbon (PAC)			Activated Coke ReACT™
	ESP	Primary FF	Secondary FF added downstream of ESP	Removal on two year cycle
Hg removed assuming coal @ 10 lb Hg/10^{12} BTU	130 lb/year	130 lb/year	130 lb/year	>130 lb/year
PAC injection rate	10 lb/10^6acfm	5 lb/10^6acfm	3 lb/10^6acfm	---
Make-up carbon	1600 ton/year activated carbon	800 ton/year activated carbon	475 ton/year activated carbon	1,000 ton/year activated coke
Disposal – not Hg laden	0	0	41,000 tons/year as ash sales	1,000 ton/year 80% coke fines, 20% flyash 41,000 ton/year as ash sales
Hg-laden disposal	46,600 tons/year	45,800 tons/year	5,475 tons/year	25 tons every two years
Hg content ppm on carbon ppm in admixture	40 ppm on PAC 1.4 ppm in admixture	80 ppm on PAC 1.4 ppm in admixture	140 ppm on PAC 12 ppm in admixture	5400 ppm

The comparison table above shows a dramatic reduction in the volume of Hg contaminated waste for the regenerated activated coke process and into a form where off-site recovery of metallic mercury from the activated coke is also possible, eliminating re-introduction of mercury to the environment.

J-Power Isogo

The Isogo repowering project which replaced 2x265 MW conventional PC boilers and pollution control (ESP, WFGD) with 2x600MW ultrasupercritical boilers and advanced pollution control represents a world class solution for clean coal. Sited in Yokohama harbor, the plant design also considered aesthetics in terms of plant appearance, including visibility at the stack. The emissions performance cited is on a par with natural gas fired facilities and the project should be of interest for U.S. energy planning at many levels.

References:

1. Steiner, P., Juntgen, H. and Knoblauch, K., "Removal and Reduction of Sulfur Dioxides from Polluted Gas Streams", Sulfur Removal and Recovery, Chapter 15, pp 180–191 *Advances in Chemistry*, Vol. 139, American Chemical Society, April 1975
2. Tsuji, K., and Shiraishi, I., "Combined desulfurization, denitrification and reduction of air toxics using activated coke", pp 549-553, *Fuel*, Vol. 76, No. 6, 1997
3. Staudt, J., Jozewicz, W. and Srivastava R., "Modeling Mercury Control with Powdered Activated Carbon", Presented at DOE/EPI/EPA/A&WMA MEGA Symposium, May 2003
4. Hirabayashi, Y., Miya, M., and Kojima, M., "Regenerative Activated Coke Technology (ReACT): A commercial multi-pollutant technology being adapted for U.S. applications"
5. Dene, C., Gilbert, J., Jackson. K., Miyagawa, S., "ReACT Process Demonstration at Valmy Generating Station", Presented at DOE/EPI/EPA/A&WMA MEGA Symposium, May 2008
6. Derrene, S., Bustard, J., McMillan, M, Chang, R., et al, "Toxecon™ Clean Coal Demonstration for Mercury and Multi-Pollutant Control at the Presque Isle Power Plant", Fuel Processing Technology, Vol. 90, No. 11, November 2009