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RECENT EXPERIENCE WITH SELECTIVE CATALYTIC REDUCTION ON POWDER RIVER BASIN COAL AND PETROLEUM COKE

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ABSTRACT:

Babcock-Hitachi K.K. has decades of selective catalytic reduction experience with a multitude of fuels. With deregulation of the American utility industry more power producers are turning to cheaper fuels, particularly Powder River Basin (PRB) coal and Petroleum Coke (Pet Coke). Included is experience the for 5 SCRs on units firing 100% Pet Coke and also a brief discussion of blending Pet Coke with bituminous coal. Just recently, our first Selective Catalytic Reduction (SCR) retrofitted on a PRB fired boiler has come on line.

INTRODUCTION:

Deregulation of the electric industry has caused electricity suppliers to seek out less costly fuels. The promulgation of clean air regulations has brought some of these fuels into question. In particular, Powder River Basin coal, while low in sulfur which allows the avoidance of costly clean up equipment, does contain a high concentration of earth metals that have been found to be detrimental to SCR catalysts.

In addition, power generators are also looking to Petroleum Coke as a low cost fuel. However, the large vanadium, content in the ash, besides causing boiler tube slagging, concentrates on the SCR catalyst surface causing increasing SO_2 to SO_3 oxidation. The additional SO_3 can be responsible for increased cold end pluggage from ammonium bisulfate, additional cold end corrosion and a "blue plume" of H_2SO_4.

The effort here is to bring to the electric utility industry the latest test results and actual experience from a leading SCR catalyst supplier.

PRB COALS:

Testing started with a characterization of PRB ash, followed with small catalyst test coupons 100 mm x 100 mm in cross section held in a cassette plus coupons 150 mm in length. Finally, testing was performed with mini-modules containing prototypically full-length plates approximately 500 mm long.

Ash Characterization:

The scanning electron microscope substantiates that the fly ash from PRB coal generally has a higher distribution of smaller particles than bituminous coal. In Figure 1 two typical PRB coal ashes are compared to a typical bituminous coal ash.

Ash Size	Typical PRB Coal	Typical Bit. Coal
> 38 μm	15 %	10 %
10 - 38 μm	30 %	80 %
< 10 μm	55 %	10 %

Table 1: Typical Ash Size Distributions: PRB and Bituminous Coals

Table 1 compares typical PRB coal ash with that from typical bituminous coal. Note that over 50% of the PRB coal ash is less than 10 μm. This means that the probability of ash adhering to the catalyst surface is greater when firing PRB coals than bituminous coals because smaller particles adhere more readily.

The typical composition of the PRB coal flyash also shows differences in composition compared to both mid-western and eastern bituminous coals as illustrated in Table 2. Of particular note is the comparison of alkaline earth metal oxides, calcium and magnesium.

Elements	PRB Coal	Mid-West Bituminous Coal	Eastern Low S Bit. Coal

NaO_2	2.1	0.6	0.4
MgO	**5.0**	**0.8**	**0.5**
Al_2O_3	16	16.6	28.0
SiO_2	21	35.6	61.2
P_2O_5	1.9	0.2	0.1
SO_3	4.4	7.5	0.6
Cl	0.05	0.08	0.1
K_2O	0.44	1.9	1.7
CaO	**33**	**8.5**	**0.9**
TiO_2	2.4	0.8	1.7
MnO	0.10	0.04	-
Fe_2O_3	10	26.9	3.7
BaO	1.6	0.05	-
PbO	0.02	-	-

Table 2: Comparison of PRB Flyash Constituents to Bituminous Coals

Coupon Testing:

Testing began in early 1998 utilizing coupon cassettes installed into PRB coal firing host utility flues. These cassettes with the 100 mm x 100 mm coupons were installed close to the economizer outlets subjecting the catalyst coupons to all the perils presented by such a location. The coupons may be subjected to higher flue gas velocities and potential damage from economizer tube leaks.

The initial test results were discouraging. The accumulation of CaO on the catalyst continually increased with service for the coupons from the various test plants. Representative data is shown in Figure 2 where the effect of velocity is readily observed. This lead to a relatively rapid decrease in catalyst activity as indicated in Figure 3.

To determine the mechanism for the catalyst activity deterioration a cross sectional analysis was performed. The results are given if Figure 4. It can be seen that the calcium accumulates near the catalyst surface, a few micrometers thick. At first this calcium takes the form of CaO but quickly becomes $CaSO_4$. This sulfate masks the porosity of the catalyst. It is within this porosity that the NOx reduction reaction takes place. Thus the activity decrease experienced.

Experience, however, indicated that the small coupons were subject to turbulent flow over their entire length. Data from bituminous coal firing indicated that the turbulent regime experienced more calcium build up than the majority of the plate that is in laminar flow. This can be evidenced from the bituminous data of Figure 5. It was therefore decided that catalyst test samples of more prototypical lengths be tested.

Mini-Modules:

A mini-module was initially defined with 150 mm long plates. These, however, were quickly judged too short so that subsequent mini-modules had catalyst of prototypical length in the flue gas flow direction but of smaller cross section. For some tests a rig utilizing a Venturi to induce the gas to flow over the catalyst was used. For other cases, a test reactor was installed across the air preheater utilizing the air preheater pressure drop to ensure gas flow over the catalyst.

Tests were conducted in several plants. In general, the plate samples showed a less pronounced activity decay than the shorter coupons, very similar to that expected for bituminous coal. In one plant it is presumed there was an economizer tube leak with the catalyst near the economizer outlet. Unlike a SCR design where the catalyst is sufficiently far from the tubes that leaking water flashes to steam long before any water reaches the catalyst, for this test case the plate samples got wet. The activity results are given in Figure 6 and plate samples, including the wet samples, are shown in

Figure 7. Unfortunately, the results were released prematurely and the erroneous conclusion put forth that Powder River Basin coal caused greatly accelerated catalyst activity deterioration and/or Selective Catalytic Reduction catalyst was not capable of withstanding the rigors of PRB coal firing.

The test results for changes in specific surface area and pore volume showed little change from the original conditions.

PRB Applications

The first SCR to go on line in a boiler firing 100% PRB coal was retrofitted on Unit 2 at the New Madrid station with the flue gas flowing to the SCR on Feb. 7, 2000. This unit is a 640 MWe cyclone fired unit with honeycomb catalyst having a 9.2 mm pitch with 80% open area.

The latest unit firing PRB coal is the Hawthorn PC unit and the SCR first received flue gas on May 16, 2001. The SCR contains a 6 mm BHK plate type catalyst with 82% open area. The Hawthorn unit had a brief outage on August 4, 2001 giving the opportunity to take some catalyst pictures. The catalyst pictures showed no signs of pluggage as evidenced in the typical picture of Figure 8.

PRB Conclusions:

Powder River Basin coal ashes contain a relatively large quantity of very fine particles. The majority of these particles are less than 10 microns in size. These ash particles also contain a higher concentration of earth metal oxides, CaO and MgO. There is a rapid accumulation of the CaO in a thin surface layer of the catalyst. This oxide combines with the SO_3 in the flue gas forming $CaSO_4$ near the surface. The calcium sulfate formed blankets the surface, masking the catalyst pores. This reduces the number of available NOx reduction reaction sites effectively reducing the catalyst's activity.

The results also indicate that higher gas velocities produce turbulent flow causing a more rapid accumulation of the calcium oxide on the surface with subsequently a rapid decrease in catalyst activity due to masking of the catalyst porosity. Thus for SCRs in a PRB fired environment it might be advantageous to clean with acoustic horn rather than sootblowers, as sootblowers cause more turbulence at the SCR catalyst.

PETROLEUM COKE:

The difficultly with Pet Coke is that it is a fuel heavy in both sulfur and vanadium. This causes continual build up of vanadium on the SCR catalyst in a heavily ladened SO_2 environment.

Pet Coke Boiler Experience:

Babcock-Hitachi currently has SCR catalyst in SCRs on five (5) boilers in operation firing close to 100% Pet Coke. These units are in Japan. The catalyst particulars for each boiler are given in Table 3 and the flue gas specifics are given in Table 4.

No.	Boiler	Operation	Catalyst Status
1	Industrial	1986	Replaced1992*
2	Industrial	1988	Add. 1995
3	IPP	1997	No Change
4	IPP	1998	No Change
5	IPP	1999	No Change

* For Improved Performance

Table 3: 100% Pet Coke Fired Boilers

No.	1	2	3	4	5
Type	Industrial	Industrial	IPP	IPP	IPP
Capacity (MWE)	-	-	≈ 150	≈ 150	≈ 150
Gas Flow (Nm3/hr)	52,300	91,200	285,000	280,000	285,000
SCR Temp. (F/C)	713/380	695/370	677/360	713/380	677/360
Inlet NOx (ppm)	240	490	300	230	300
Outlet NOx (ppm)	130	150	9	75	9
DeNOx Eff. (%)	46/68	69	97	67	97
NH3 Slip (ppm)	10/5	10	3	5	3
O2 (%)	3.6	3.9	3.5	3.6	3.5
SOx (ppm)	2,500	3,050	4,450	5,800	4,450
SO3 (ppm)	25	50	90	N/A	90
Dust (gm/Nm3)	1.4	1.4	2.6	3.0	2.6

Table 4: Pet Coke Fired Boilers' Flue Gas Conditions

Initially the catalyst activity tends to remain flat as the build up of vanadium on the catalyst compensates for the catalyst degradation. Eventually, the alkali poisons in the flue gas cause an activity decrease. This build up continues causing the SO_2 to SO_3 oxidation rate to continuously increase indefinitely with oxidation rates exceeding about 10 times those normally found in practice. The SCR catalyst can be rotated in other service to maximize its life without excessive SO_2 oxidation.

Pet Coke Blends:

Current studies with blending Pet Coke indicate that the mixing of Pet Coke with bituminous coal negates the ill effects of SO_2 oxidation provided that the percentage of Pet Coke is sufficiently low. Studies are continuing to determine the upper limits for blending without excessive SO_2 oxidation.

Pet Coke Conclusions:

The firing of 100% Pet Coke requires considerable catalyst replacements unless the catalyst can be rotated through other service to prevent excessive SO_2 to SO_3 oxidation rates.

It has been found, however, that blending the Pet Coke with bituminous coals can prevent increasing oxidation rates. Babcock-Hitachi is striving to determine the maximum Pet Coke blend that is permissible without ever increasing SO_2 oxidation rates.

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Typical PRB Coal Ash # 1 | Typical PRB Coal Ash # 2 | Typical Bituminous Coal Ash

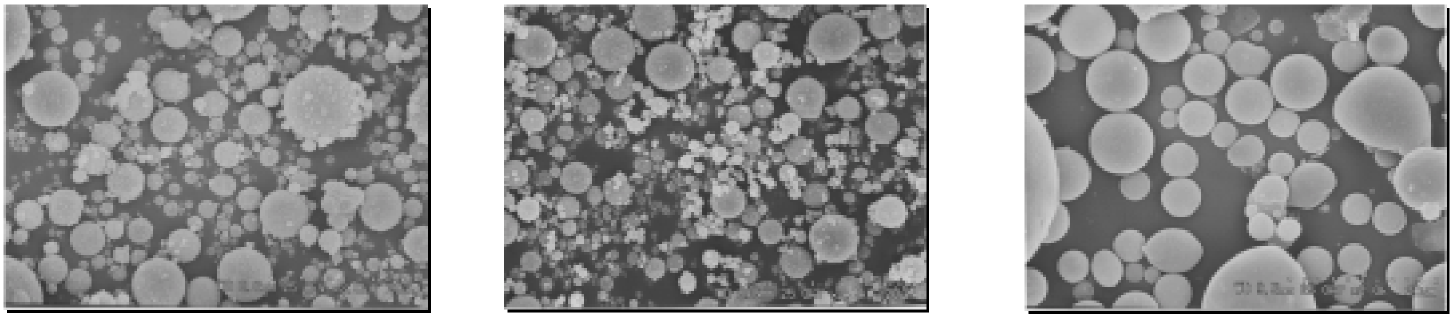

Figure 1: Comparison of Ash Size Distribution

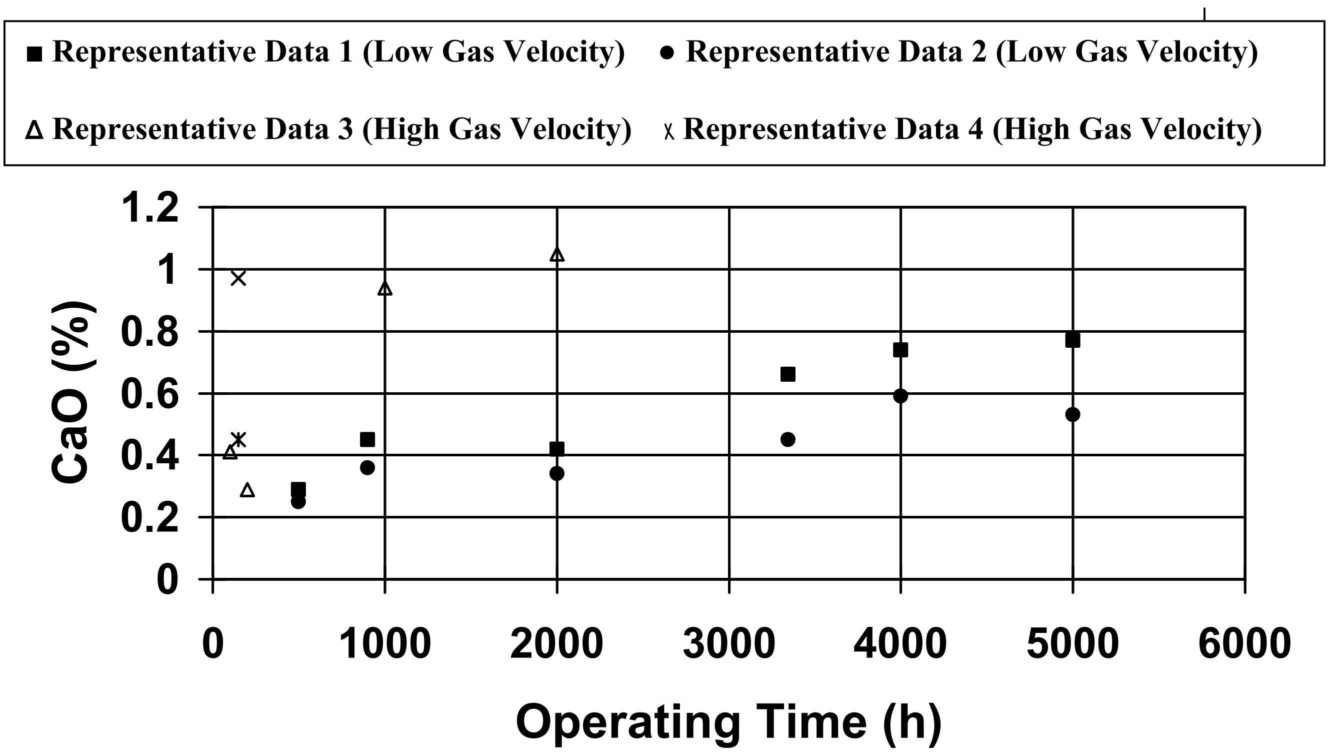

Figure 2: CaO Accumulation

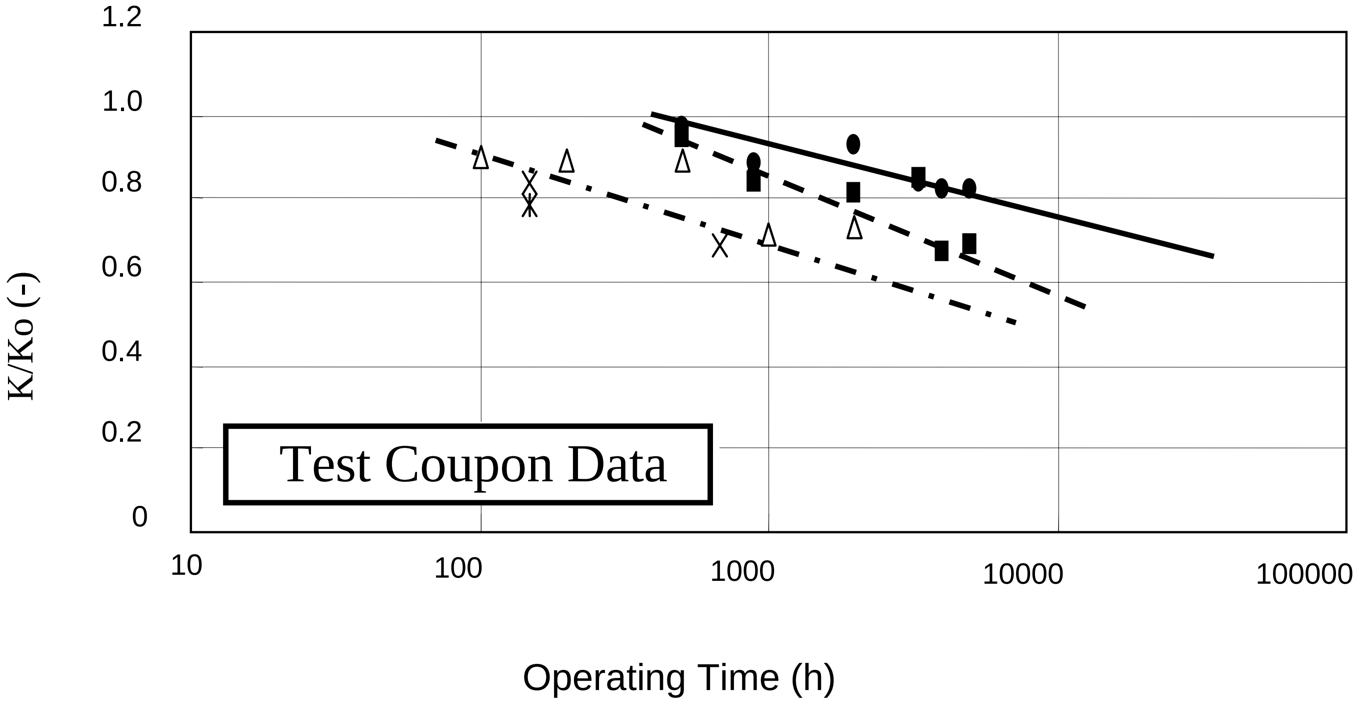

Figure 3: Coupon Activity with Operating Time

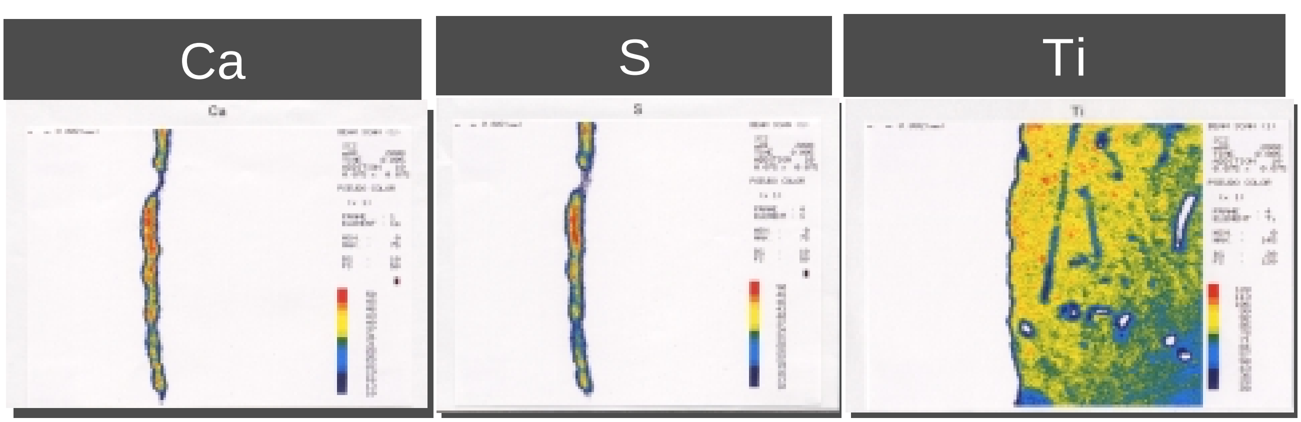

Figure 4: Surface Accumulation of Ca and S
(Ti included for Comparison)

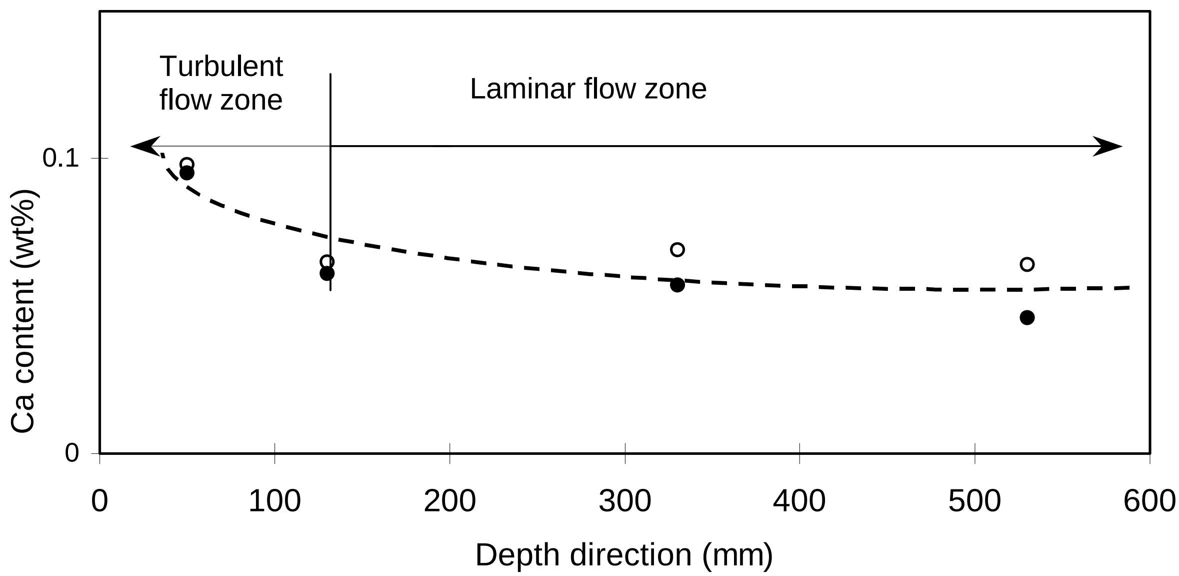

Figure 5: Calcium Content Distribution over Catalyst Depth (Direction of Flue Gas Flow)

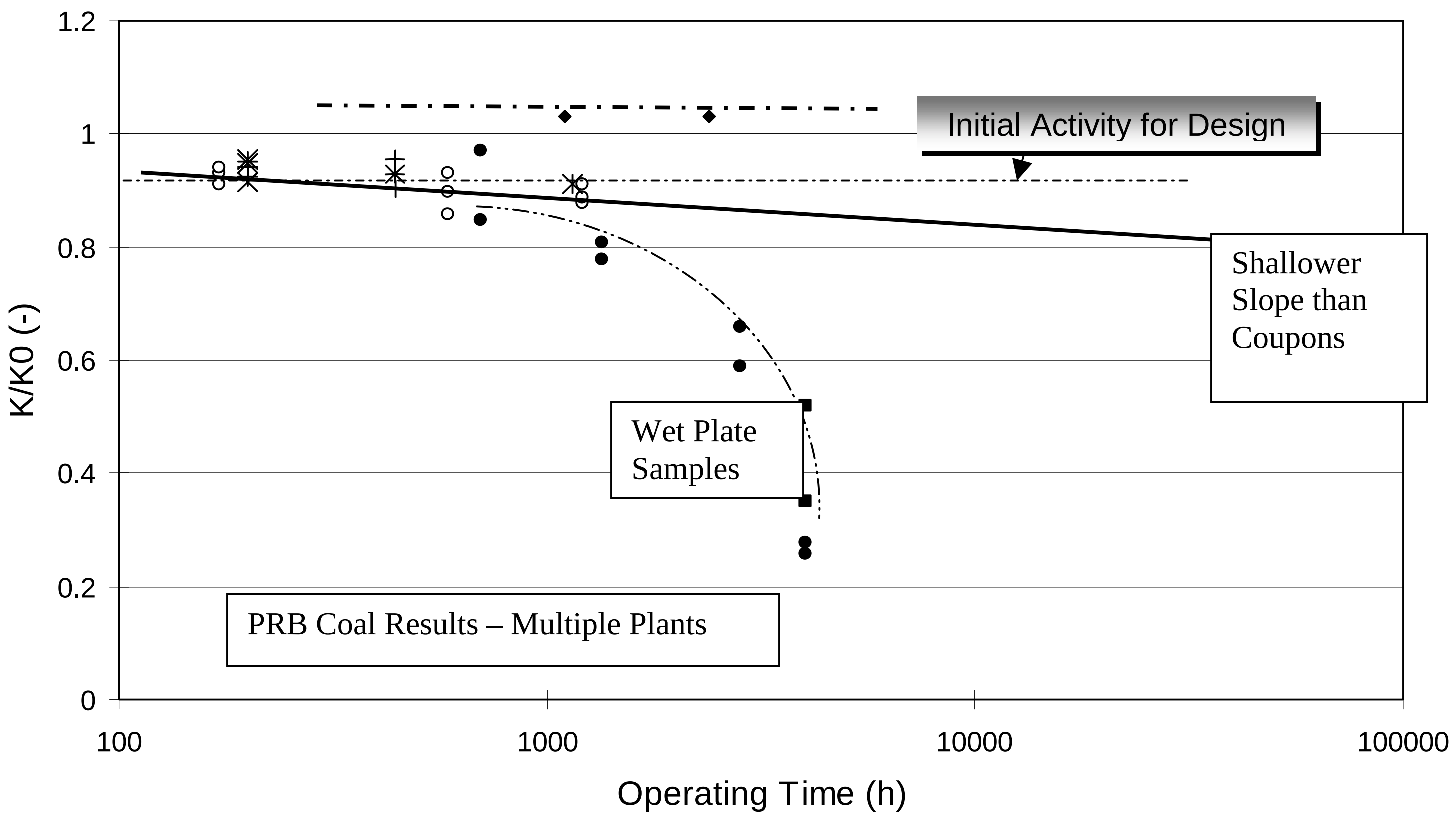

Figure 6: Mini-Reactor Plates - Activity verses Time

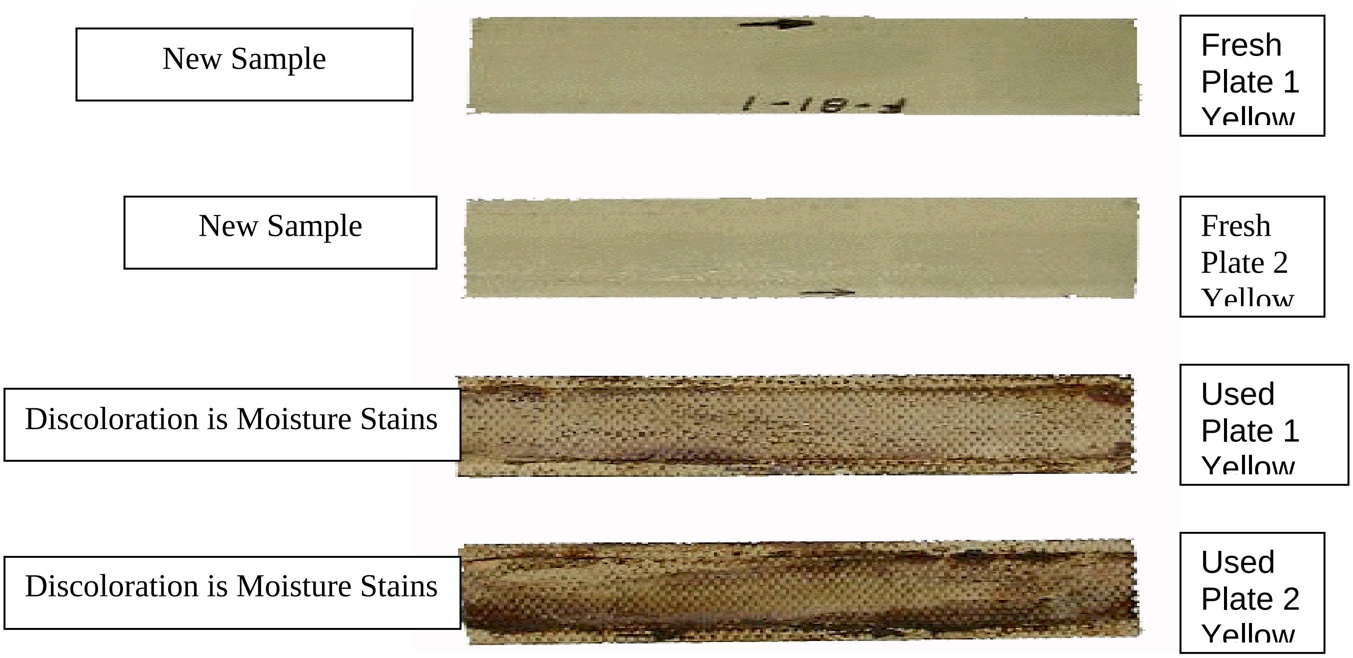

Figure 7: Mini-Reactor Catalyst Samples Photos

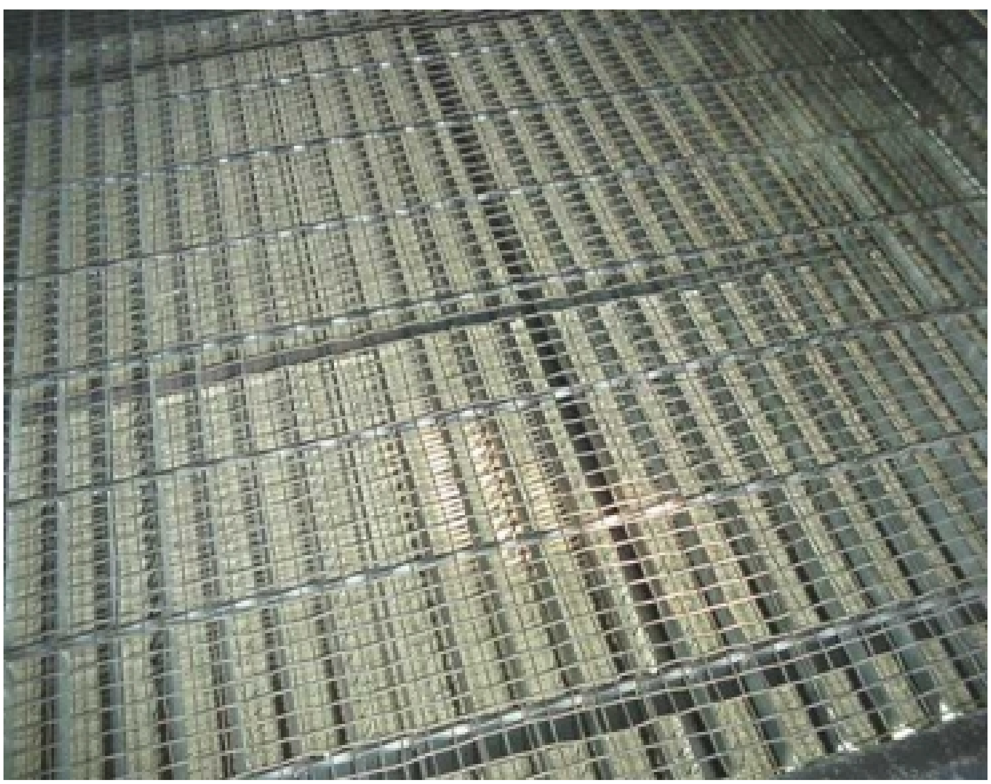

Figure 8: Hawthorn SCR Catalyst After ≈ 3 Months Service

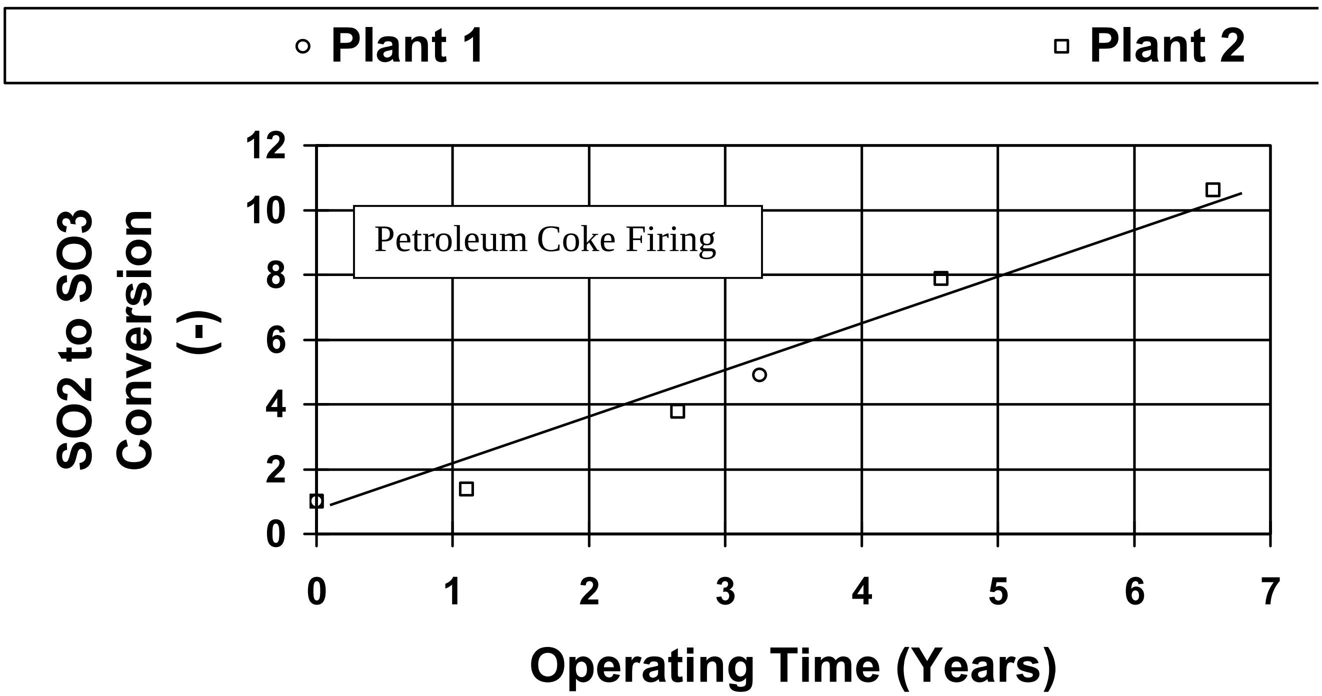

Figure 9: SCR Catalyst SO_2 to SO_3 oxidation with Time