

Laboratory and Vehicle Demonstration of “2nd-Generation” LNT + in-situ SCR Diesel Emission Control Systems

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ABSTRACT

Diesel NO_x emissions control utilizing combined Lean NO_x Trap (LNT) and so-called passive or in-situ Selective Catalytic Reduction (SCR) catalyst technologies (i.e. with reductant species generated by the LNT) has been the subject of several previous papers from our laboratory [1 - 2]. The present study focuses on hydrocarbon (HC) emissions control via the same LNT+SCR catalyst technology under FTP driving conditions. HC emissions control can be as challenging as NO_x control under both current and future federal and California/Green State emission standards. However, as with NO_x control, the combined LNT+SCR approach offers advantages for HC emission control over LNT-only aftertreatment. The incremental conversion obtained with the SCR catalyst is shown, both on the basis of vehicle and laboratory tests, to result primarily from HC adsorbed on the SCR catalyst during rich LNT purges that reacts during subsequent lean engine operation.

INTRODUCTION

Diesel emissions control at the lowest levels required by federal and California standards at full useful life will create significant challenges for diesel aftertreatment systems. Previous studies have focused extensively on NO_x control given the challenges of reducing NO_x to N₂ under the normal lean engine operating conditions of diesel engines. To date, the leading aftertreatment technologies have involved either lean NO_x trapping [3, 4, 5, 6, 7, 8, 9] or selective catalytic reduction [10, 11, 12, 13, 14, 15, 16, 17] (either with HC species or urea). Over the past several years, a number of studies (including several from our laboratory) have reported on LNT+SCR systems which utilize the SCR catalyst in a “passive” or “in-situ” mode where the reductant required to convert NO_x that breaks through the LNT is generated over the LNT during

NO_x purge or reduction events [1-2, 18, 19, 20, 21]. Our previous studies focused on LNTs containing relatively low platinum group metal (PGM) loadings and improved durability compared to earlier formulations. The SCR catalysts were primarily Cu-zeolite formulations identical to those used in urea-SCR vehicle applications.

During the course of our previous studies, we observed that non-methane hydrocarbon emission control at tailpipe levels approaching federal Tier 2 - Bin 2 or California proposed LEV-III standards over the FTP drive cycle is at least as challenging, and in some cases more challenging, than NO_x control. Moreover, efforts to reduce NO_x emissions - both directly out of the engine and at the tailpipe - can result in increases in HC emissions, and vice-versa. Especially for LNT-based aftertreatment control, the LNT purge must be managed carefully to achieve effective NO_x clean-out without HC breakthrough. In the present study, we focus specifically on NMHC conversion in LNT+SCR aftertreatment. In particular, we provide evidence that the SCR catalyst enhances NMHC conversion over levels obtained with the LNT by itself.

EXPERIMENTAL

LABORATORY EXPERIMENTS

The laboratory setup, instruments, gas compositions, and evaluation and aging procedures are the same as previously reported [1-2, 9]. The catalysts were 25 mm diameter by 25 mm long cores cut from larger monoliths (cordierite with 400 cells per square inch and 6.5 mil wall thickness). The catalysts were tested in a quartz tube reactor contained in a tube furnace. Gases were blended synthetically (see Table 1 for composition) and fed to the reactor at flow rates corresponding to a volumetric

space velocity of 30K hr^{-1} , which is representative of driving speeds found in the FTP. Catalyst temperatures were measured at the inlet (6mm in front of the sample), mid (middle of the 25 mm inch sample core), and the outlet (6mm after the sample). Experiments with both LNT and SCR catalyst cores utilized 25 mm samples of each separated by 6mm. All catalyst temperatures reported herein refer to the inlet temperature (unless noted otherwise).

The laboratory experiments utilized a V&F Airsense chemical ionization mass spectrometer, Midac heated FTIR (4m cell), and a Horiba Mexa 9100 Hegr gas bench consisting of a chemiluminescent analyzer (NO_x , NO), combined flame ionization (THC)/Magneto-pneumatic (O_2) analyzer, and non-dispersive infrared analyzer (CO and CO_2). Gases to the mass spectrometer and analyzer bench were passed through heated sample lines and diluted with N_2 in a ratio of about 1:3 to avoid water condensation. Heated, undiluted “raw” gas was fed to the FTIR. For the majority of testing, a standardized set of gas compositions was used (Table 1). The gas runs in the lean condition for a period of time, then switches to the rich composition for a different period of time, and this cycle repeats. Typical duty cycle used in these experiments was 60 seconds lean and 5 seconds rich (60/5).

Table 1. Standard gas composition

Gas	Lean	Rich
CO	0%	3%
H_2	0%	1%
C_3H_6	0%	5000 ppmC1
NO_x	200 ppm	200 ppm
O_2	10%	1%
CO_2	5%	5%
H_2O	5%	5%
λ	1.96	0.92

These gas compositions are not entirely representative of diesel exhaust. NO_x was supplied exclusively as NO at a relatively high level for a part load operating mode, so as to better discriminate between catalyst formulations. A 3:1 ratio of $\text{CO}:\text{H}_2$ was used. We utilized propylene (C_3H_6) and ethylene as our HC - typical of light cracked hydrocarbons in diesel exhaust but not representative of larger unburned fuel species.

All catalysts were provided by one of Ford’s catalyst suppliers. Catalysts are identified only by their generic type (e.g., Cu-zeolite SCR or LNT) and overall PGM loadings (LNTs) to protect supplier confidentiality. The LNTs used in this work are “New” generation (reference last year’s SAE). The new LNT formulations have lower desulfation temperatures ($680\sim 700^\circ\text{C}$) than the old generation ($750\sim 800^\circ\text{C}$), which translates into lower peak aging temperatures and better durability (as described in [1]).

The oxygen-storage-capacity (OSC) of each sample was determined using $1.0\%\text{CO}/0.5\%\text{O}_2$ alternating pulses. The detail of the set-up has been described in a previous report [22]. For this work, a core of $25.4\text{ mm L} \times 25.4\text{ mm D}$ was placed in a quartz reactor and heated to the desired temperature in $0.5\%\text{O}_2$. After the temperature was stabilized, alternative pulses of $1\%\text{CO}$ and $0.5\%\text{O}_2$ in He were passed through the catalyst. He pulses of 10-s duration were interspersed between the 50-s pulses to purge any residual CO or O_2 in the gas phase. A quadrupole mass analyzer (Hiden RC20) was used to monitor mass 28 (CO), mass 32 (O_2), mass 40 (Ar as the internal standard), and mass 44 (CO_2) in the reaction effluent. The OSC was calculated based on the amount of CO consumption or CO_2 production during the CO pulse, or O_2 consumption during the O_2 pulse.

VEHICLE TESTING

Two vehicles were tested with similar configurations of the aftertreatment system. The first vehicle tested was a production 2005 MY Land Rover (LR3) diesel vehicle that was Euro 3 emission compliant. This vehicle was equipped with a twin turbocharged, common rail direct injected 2.7L V6 (Lion) diesel engine. The front drive shaft was disconnected to convert the original all-wheel-drive system to rear-wheel drive for emission testing on a single roll chassis dynamometer. The powertrain control system was originally modified for lean NO_x trap aftertreatment system development, but was subsequently adapted for evaluation of the LNT+SCR system as depicted in Fig. 1. The catalyst information is shown in Table 2. Both the LNT and SCR were hydrothermally aged at 750°C for 64 hours before installation. The vehicle inertia weight was set to 3780 lbs on the chassis dynamometer to simulate the power to weight ratio equivalent to a light duty diesel truck. The second vehicle equipped with the LNT+SCR system was a non-production 4.4L V8 TDI light duty pickup truck. The inertia weight was set to 5750lbs on chassis dynamometer for this vehicle. The catalysts in this truck are arranged in the same order as on the LR3 (DOC plus LNT and SCR followed by catalyzed DPF). The catalyst information on this truck is shown in Table 3. Three Horiba modal emission benches and two modal FTIR (Horiba 4000 and 6000 with 2.4 meter path lengths) were used to measure the sec-by-sec emissions at various sample locations labeled in Fig. 1 below.

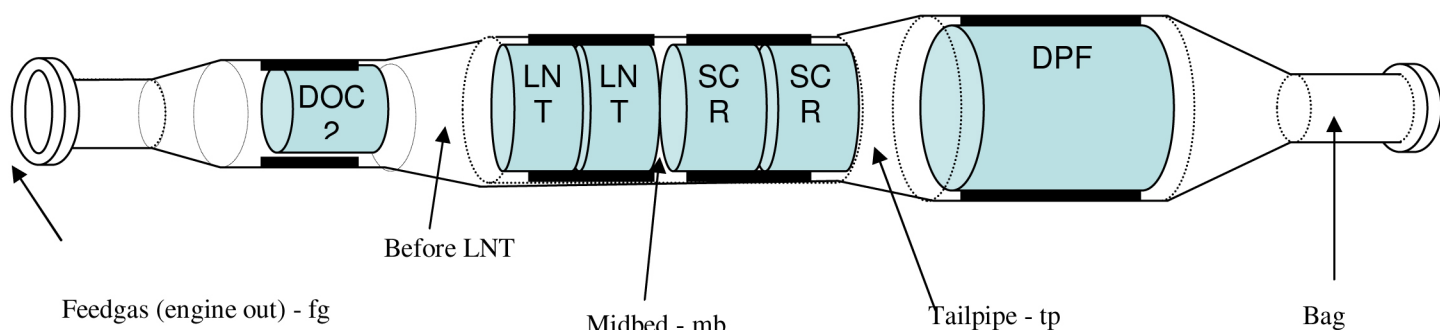


Fig. 1. Schematic diagram of the catalyst system layout used on both the LR3 vehicle and the 4.4L light-duty truck. Catalyst details are given in Tables 2 and 3, respectively. Note that the LR3 has a small metallic DOC (see Table 2) located upstream of DOC 2 that is not shown in the diagram.

Table 2. Catalyst configurations on the Land Rover (LR3) vehicle

Component	Load	Dia. x Length (in)	Calc. Vol (L)	Engine Swept V	Material	Cell CPSI / Wall
DOC 1*	70g/ft ³	3" x3"	-	-	Metallic	-
DOC 2	70g/ft ³	4.66" x 3"	0.84	31%	Ceramic	400 / 6 mil
LNT	85g/ft ³	2 – 5.66"x3.5"	2.88	107%	Ceramic	400 / 6 mil
SCR	-	2 – 5.66"x3.5"	2.88	107%	Ceramic	400 / 6 mil
cDPF	20g/ft ³	7.5" x 8 "	6.0	222%	SiC	200 / 15mil

DOC1 is close coupled to engine exhaust manifold.

Table 3. Catalyst dimensions of the 4.4L V8 Mockup light duty truck

Component	PGM Load	Dia. x Length (in)	Calc. Vol (L)	Engine Swept V	Material	Cell CPSI / Wall
DOC	90g/ft ³	2 - 4.66" x 4"	2.23	51%	Ceramic	400 / 6 mil
LNT	85g/ft ³	7.5" x 5"	3.6	82%	Ceramic	400 / 6 mil
SCR	-	8" x 6"	4.94	112%	Ceramic	400 / 6 mil
cDPF	5g/ft ³	8" x 8 "	6.59	150%	SiC	200 / 15mil

The regulated species (THC, CO, NO_x, NMHC, CO₂, O₂) were measured and reported on a sec-by-sec basis using Horiba 7000 modal emission analyzer systems. Additional species were measured using Horiba 4000 and 6000 model FTIRs including NO₂, N₂O, NH₃, HCHO, C₂H₂, C₂H₄, and C₃H₆. Special consideration was taken to reduce the hang-up of NH₃ and other hygroscopic molecules of interest in the FTIR sampling system: The inline heated filter elements were chosen for their low absorptivity for NH₃. Finally, the entire sampling train from the exhaust probes to the analyzer were preheated and maintained to at least 130°C.

RESULTS & DISCUSSION

VEHICLE FTP PERFORMANCE OF LNT+SCR SYSTEMS

The primary reason for adding the SCR catalyst downstream of the LNT is to convert NO_x that breaks through the LNT. This is illustrated in Fig. 2, which is a bar graph of NO_x modal emissions measured at different points in the F-150 exhaust system for two repeat FTP tests run with rich trap regenerations. Conversions of NO_x across the SCR catalyst are 33 and 64% for the two runs, respectively. Similar bar graphs are shown in

Figs. 3 and 4 for NMHC emissions - Fig. 3 without rich trap regenerations and Fig. 4 with regenerations. As expected, the bulk of the NMHC conversion occurs across the DOC and LNT catalysts; however, in all cases, the SCR catalyst converts two-thirds or more of the NMHC that breaks through the LNT. Overall NMHC emission levels are higher at each sampling point in the runs made with rich regenerations (Fig. 4), reflecting the rich purge contribution to the total emissions. This is seen more clearly in the cumulative NMHC emissions plotted in Fig. 5 for one of the runs made without rich regenerations, and in Fig. 6 for one of the runs made with rich regenerations. In comparing the two figures, the higher emissions of the run made with rich regenerations result primarily from step increases in engine-out emissions associated with the four purge events at roughly 200, 800, 1570 and 1750 s). The rich NMHC spikes cannot be totally mitigated by the combined aftertreatment components, although it is clear from Fig. 6 that the SCR catalyst dampens considerably the LNT NMHC breakthrough occurring during the four regeneration events. The SCR catalyst also plays a role in NMHC emissions control during engine warm-up where it can be seen in both Figs. 5 and 6 that NMHC which initially breaks through the LNT appears to store on the SCR catalyst and react (rather than desorb) as the SCR catalyst warms up.

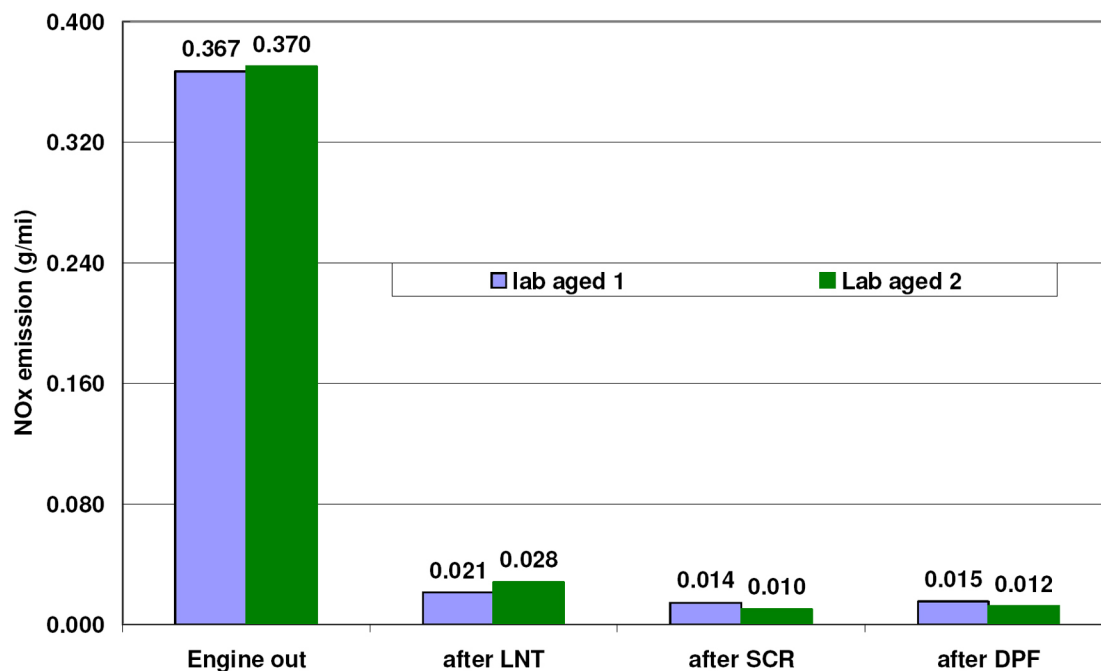


Figure 2. NO_x emissions out of engine, after the LNT, after the SCR and after the DPf (i.e., tailpipe) over 2 FTP75 tests (F150 with four rich regenerations for each test)

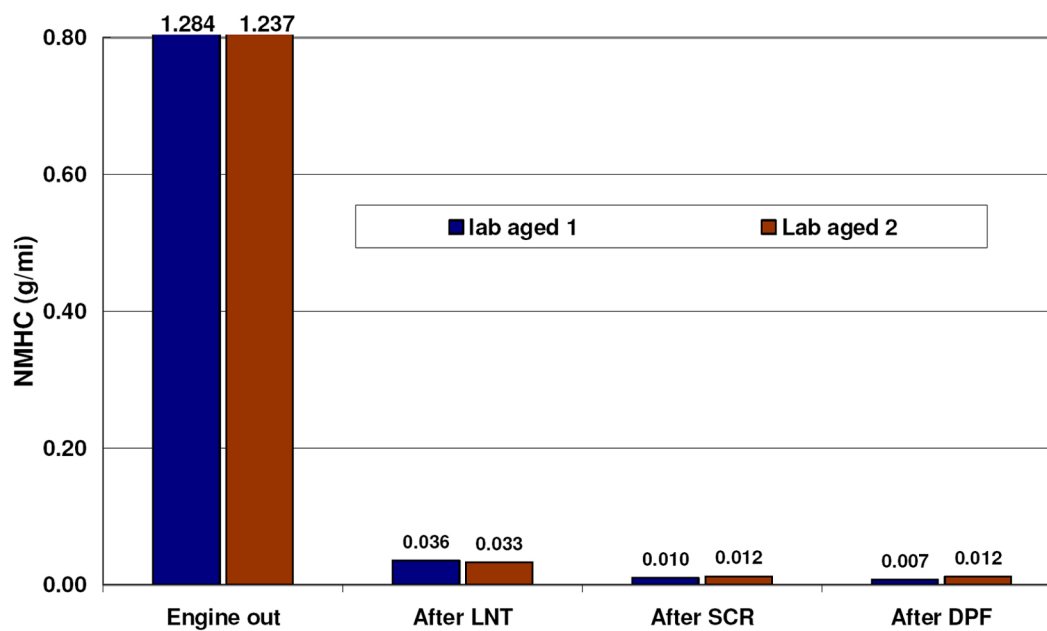


Figure 3. NMHC emissions out of engine, after LNT, after SCR, and after DPF (i.e., tailpipe) over 2 FTP75 tests (F150 without rich regeneration in each test) under lean only conditions.

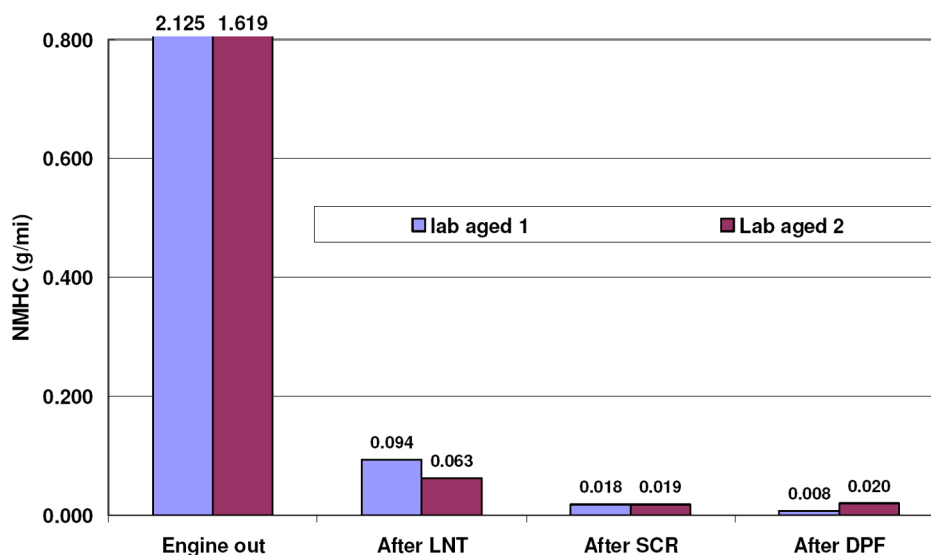


Figure 4. NMHC emissions out of engine, LNT, SCR and DPF in FTP75 test (with four rich regenerations)

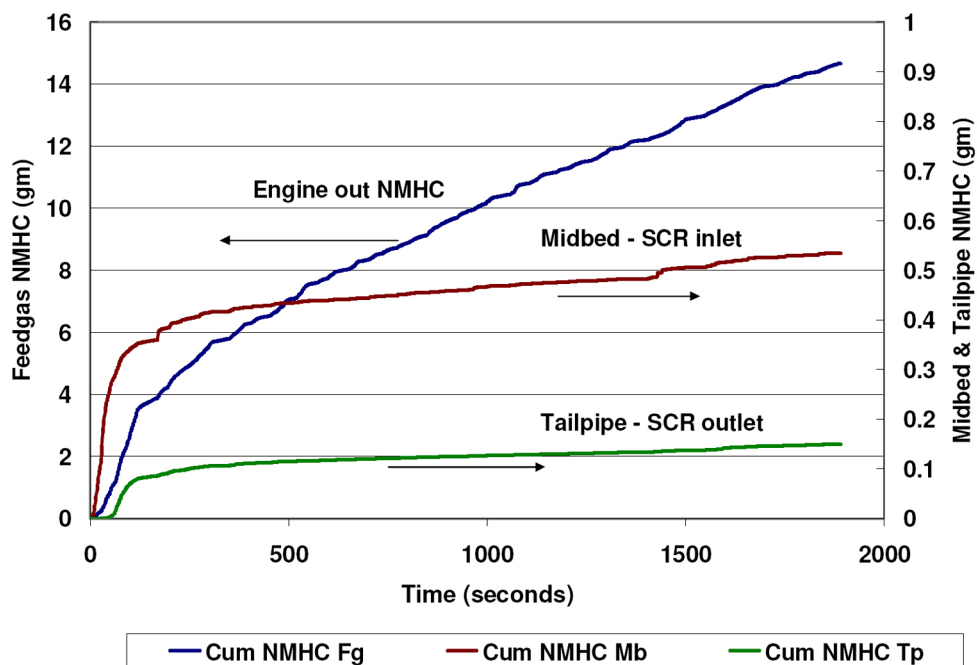


Figure 5. Cumulative NMHC emissions at different locations: engine out, SCR inlet and SCR outlet over FTP 75 test cycles without rich regenerations

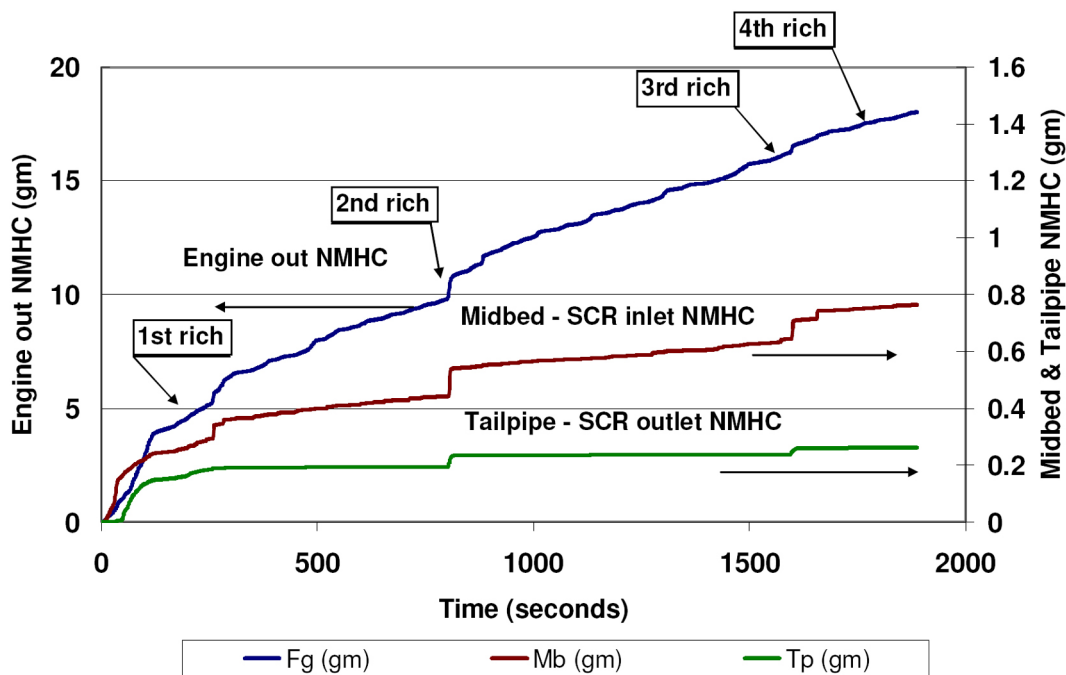


Figure 6. Cumulative NMHC emissions at different locations: engine out, SCR inlet and SCR outlet over FTP 75 test cycles with 4 rich regenerations as indicated (approximately 200s, 800s, 1570s & 1750s)