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Predicting SO₃ Levels Along Utility Gas Cleaning Systems

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ABSTRACT

This paper introduces a combined homogeneous and heterogeneous SO₃ production mechanism to determine whether or not particular flue gas cleaning conditions promote SO₃ condensation anywhere upstream of the ESP. This mechanism was validated against measurements at different locations along the gas cleaning systems at fourteen power plants representing the entire range of coal-S, furnace stoichiometry, and gas cleaning conditions found in commercial applications. The SO₃ production mechanism was then integrated into previously validated Hg transformation mechanisms to account for inhibition of Hg oxidation and removal due to SO₃ condensation on fly ash, UBC and activated carbon. This analysis was subsequently used to interpret Hg removals for about two dozen test measurements at Plant Daniel. These tests included different coal blends, ACI concentrations, conventional and brominated activated carbons, and SO₃ concentrations. The simulations clearly identified the tests affected by SO₃ interference and predicted the Hg removal by ACI to within 15 % of the test measurements for 19 of the 22 tests at this site.

INTRODUCTION

Activated carbon injection (ACI) into flue gas is currently the most important strategy for Hg capture in utility gas cleaning systems, especially for plants firing low rank coals which have inherently low concentrations of Cl. Several tests reported in NETL's Phase II Hg field-testing database indicated that SO₃ in the flue gas, either from the conversion of inherent SO₂ or from the addition of SO₃ as a flue gas conditioning agent, significantly diminishes Hg capture by activated carbon sorbents. The testing did not demonstrate that a threshold SO₃ concentration determined whether or not SO₃ interference would come into play. Compounding matters, measurements of SO₃ concentrations are subject to large uncertainties and are almost never reported with Hg speciation in field tests. Consequently, we developed a mechanism for SO₃ production and integrated it into reaction mechanisms for Hg transformations to quantify the inhibitory effect of SO₃ on Hg capture by unburned carbon (UBC) and ACI. This paper evaluates the simulation results with a suite of SO₃ measurements along full-scale cleaning systems, and with measured Hg removals in ACI applications at one power plant.

REACTION MECHANISMS

SO₃ Production Mechanism

The mechanism for SO₂ oxidation describes the production of SO₃ from the furnace convective passes through the particle collection device (PCD) and consists of a collection of homogeneous and heterogeneous reaction mechanisms for distinct segments of a utility gas cleaning system. Sulfur dioxide begins to oxidize in the gas phase as flue gas moves through the convective passes. For this stage, we use the elementary reaction mechanism with 134 reactions involving 30 species reported by Yilmaz et al.¹ with no modifications to any of the rate parameters. The SO₃ production mechanism can shift to a heterogeneous mechanism on flyash while flue gas moves through the final superheaters and the economizer. Since the contribution from this stage has been related to the Fe content of flyash, we developed a closed-form analytical expression for the heterogeneous rate from the lab tests of Jorgensen et al. on SO₂ oxidation over Fe₂O₃.² This rate depends on the concentrations of SO₂ and O₂ in the flue gas, as well as the mass fraction of Fe₂O₃ in the flyash. However, this heterogeneous contribution is very small unless both the ash content and the pyrite fraction are exceptional.

A second heterogeneous mechanism oxidizes SO₂ into SO₃ along SCR catalysts. We developed the rate for this stage from the mechanism reported by Svachula et al.³, which has already been validated with extensive lab-scale data and used to accurately predict SO₃ production from full-scale utility SCRs. This heterogeneous rate depends on the concentrations of SO₂ and O₂, as expected. It also depends on the concentrations of moisture, NH₃, and NO, because both moisture and NH₃ inhibit SO₃ oxidation, whereas NO promotes it. Since NH₃ is always the deficient reactant in utility deNO_x applications, the SO₂ oxidation rate accelerates while the NH₃ concentration decays along the SCR catalyst, and becomes fastest through the trailing section of monolith.

Once the SO₃ has been produced as a vapor species, it may condense within the air preheater (APH) depending on the acid dew point of the flue gas. In the calculations, we evaluate dew points from the APH inlet through the PCDs with a dew point correlation⁴ and the assigned flue gas composition. As soon as the gas temperature falls below a dew point, sufficient SO₃ is condensed onto flyash to reduce the dew point to the local gas temperature. These incremental condensations occur while the flue gas moves through the APH and into the PCD, provided that the dew point exceeds the local gas temperature. Otherwise, no SO₃ condenses to interfere with Hg adsorption. In the heterogeneous mechanism for Hg/Cl chemistry, the population of carbon sites that can be chlorinated and therefore participate in adsorption of both elemental Hg (Hg⁰) and oxidized Hg (Hg²⁺) is reduced in proportion to the amount of condensed SO₃. When the condensate completely covers the chlorinated site population, the interference reaches the saturation limit for monolayer SO₃ coverage.

Hg Transformation Mechanism

According to the established phenomenology for Hg transformations via Cl chemistry,

suspended UBC is chlorinated while flue gas moves through the back-end heat exchangers, and Hg^0 oxidizes on the chlorinated sites at faster rates for progressively greater Cl levels in the flue gas. This stage of the in-flight heterogeneous chemistry is limited by the Hg^0 adsorption rate, so Hg^{2+} is produced but there is little accumulation of Hg on UBC particles in the back-end section. Generally, Hg^0 oxidizes even faster along SCR catalysts than on UBC if the Cl levels are moderate or higher, although the oxidation rates are affected by the catalyst formulation and several SCR operating conditions⁵. Downstream of the SCR, the chemistry shifts back to the in-flight mechanism on UBC which, in turn, shifts to desorption control when the flue gas is cooled by the APH. In this regime, adsorbed Hg species accumulate on UBC as particulate Hg (HgP) and are ultimately recovered in PCDs along with flyash. What little chemistry occurs at the low temperatures of PCDs perturbs the proportions of Hg^0 , Hg^{2+} , and HgP until enough UBC has been removed from the flue gas to quench the chemistry completely. Nearly all the Hg^{2+} vapors will be dissolved and retained in the FGD wastewater, while the Hg^0 vapors pass into the smokestack.

This phenomenology has been implemented with a 168-step homogeneous mechanism and a 6-step heterogeneous mechanism for Hg/Cl chemistry⁶, and was recently expanded for Hg/Cl/Br chemistry⁷. The basic heterogeneous Cl mechanism was independently validated with Hg transformation data on whole coal-derived flue gas with suspended flyash and UBC first at lab-scale⁸; then at pilot-scale⁹; then with a field-test database that represents more than 50 field tests in various full-scale gas cleaning configurations⁶. At this point it has been used to interpret over 100 sets of Hg speciation data from full-scale field tests, including nearly all the tests in the Phase I and II NETL Hg testing program¹⁰.

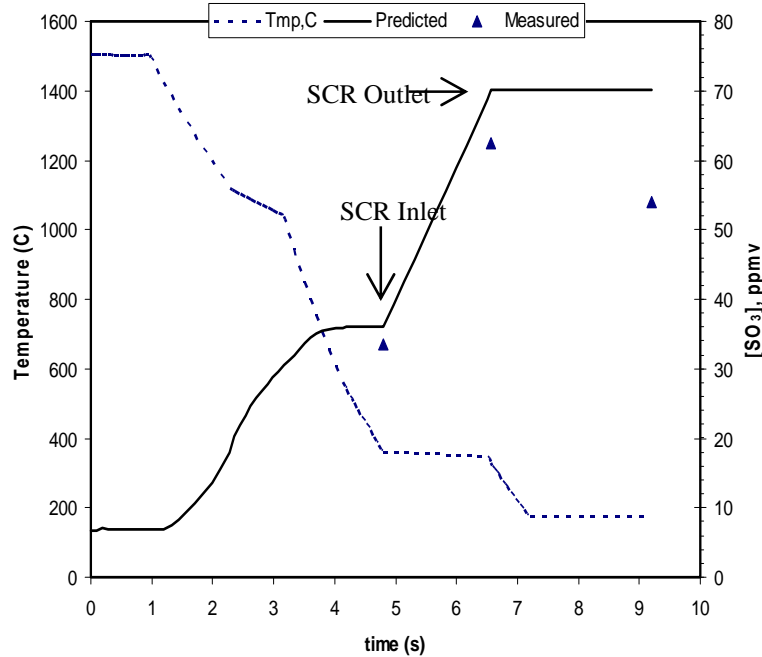
VALIDATION OF THE SIMULATIONS RESULTS

Validation of the SO₃ Production Mechanism

To validate the predictions from the SO₃ production mechanism, a database of SO₃ concentrations in coal-derived flue gas was compiled from literature including NETL field-tests on Hg speciation and/or SO₃ control. It comprises fourteen test measurements from thirteen full-scale cleaning systems. Of the fourteen tests, twelve tests were on units firing bituminous coals and one test each was on a unit firing a subbituminous coal and a subbituminous/bituminous blend. Ten tests included an SCR in the gas cleaning system, of which five tests reported SO₃ concentrations at both the SCR inlet and outlet while three and two tests, respectively, reported SO₃ concentrations at only the SCR outlet and only SCR inlet. Three of the eight tests which reported a measured SO₃ concentration at the SCR outlet did not satisfy the input data requirements for modeling SO₃ production across an SCR. For these three tests, the predicted SO₃ was compared with the measured value only at the SCR inlet. For the tests that did not involve an SCR, two tests each reported SO₃ concentrations at the economizer outlet/APH inlet and APH outlet/ESP inlet. Test measurements beyond the ESP inlet were not used for validation purposes.

The SO₃ database covers the full range of coal-S (from 0.4 to 4.8 daf wt. %) and furnace stoichiometry in commercial power plants. Note, however, that in most cases test-specific

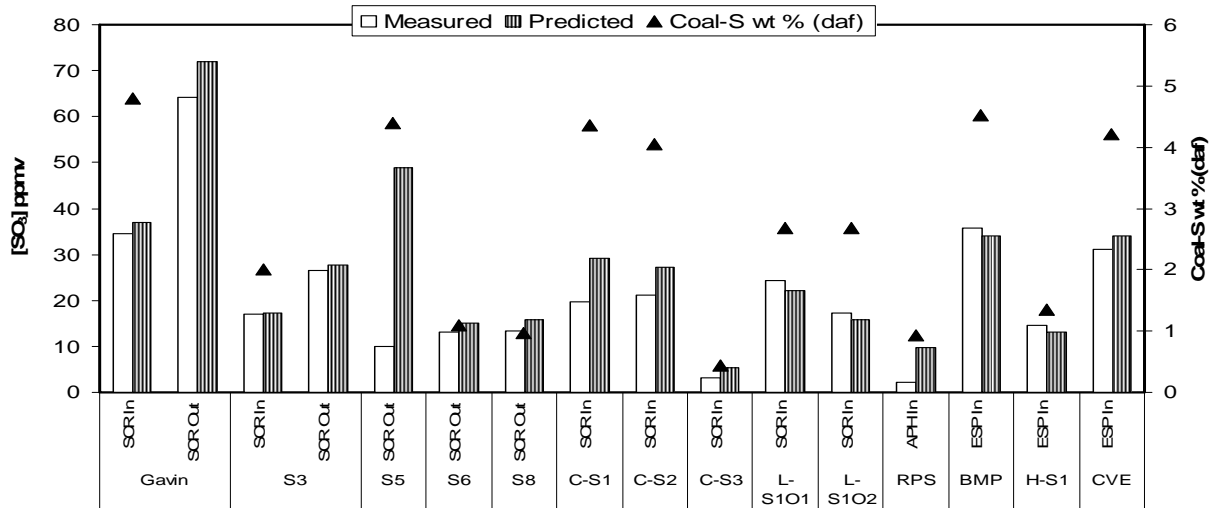
Figure 1. Predicted SO₃ concentration along the gas cleaning system at Gavin compared with measured values (▲) on a wet basis at the actual O₂ level. The thermal history appears as the dashed line segments.



coal properties including coal-S were not available and the calculations therefore used nominal values. Some tests at the sites which had test-specific coal-S measurements were discarded because the measured SO₃ concentrations either fell below the detection limit or were deemed too low by the testing teams. The economizer O₂ varied from 2.1 to 4.2 % with most cases between 3.3 and 3.7 %. Two independent tests at one site reported SO₃ concentrations at the SCR inlet for economizer O₂ levels of 2.1 and 3.5 %. The effect of O₂ on SO₃ formation factors into our simulations of these tests. No economizer O₂ levels were reported for tests C-S1, C-S2 and C-S3. These tests were simulated at an O₂ level of 3 % because the measurements were normalized to this level.

A simulation of the test case at Plant Gavin appears in Fig. 1 showing the predicted formation of SO₃ from the furnace through the APH. Gavin fires a bituminous coal with 4.8 daf wt % S at a furnace stoichiometry that gives 3.5 % O₂ at the economizer. Since flue gas temperatures were reported only from the economizer outlet onwards, the calculations impose our default thermal history for the upstream sections. SO₂ begins to oxidize in the convective passes, and continues to oxidize into the economizer. The SO₃ concentration increases through the back-end heat exchangers, but reaches a plateau near the economizer inlet, well-upstream of the SCR inlet. Along the SCR catalyst, SO₂ oxidizes at the fastest rate of all to double the SO₃ concentration. The predicted SO₃ concentrations at the SCR inlet and outlet of 36 and 72 ppmv compare well with the measured values of 33.5 and 62.4 ppmv, respectively. There are no channels for SO₃

Figure 2. Measured (open bars) and predicted (hatched bars) SO₃ concentrations at various sampling locations on a wet basis corrected to 3 % O₂. Coal-S values (▲) in daf wt % are indicated on the right axis.



production downstream of the SCR so the flue gas SO₃ level remains constant until the flue gas reaches the acid gas dew point. For this cleaning system, the flue gas temperature was always above the calculated acid dew point of 153.4°C. The reason for the drop in the measured SO₃ concentration at the APH outlet is therefore unclear.

The predicted SO₃ concentrations for all cases in the SO₃ validation database are compared with measured values in Fig. 2. Five cases with predictions across SCRs from four vendors appear on the left side. At present, an identical set of SO₂ oxidation rate parameters is used for the different vendors. Vendor-specific parameter sets, similar to the sets we use for Hg⁰ oxidation, will be specified as additional datasets become available. The predicted SO₃ concentrations match the measured values at all sites except S5 and, perhaps, RPS. All the predicted concentrations at SCR inlets are accurate. The predicted enhancement of SO₃ across SCRs is accurate for all sites except S5, where it was over-predicted. And the SO₃ levels at the three ESP inlets are also accurate. The measurements at L-S1 indicate a 29.3 % reduction in SO₃ as the economizer O₂ was reduced from 3.5 to 2.1 %, versus a predicted reduction of 29.4 %.

Minor discrepancies at C-S1 and C-S2 are attributed to the omission of economizer O₂ levels in the test report which, as seen in L-S1O1 v. L-S1O2, can account for several ppm of SO₃. The only major discrepancy in the validation is at S5 where the predicted SO₃ concentration of 49 ppm at SCR inlet is significantly higher than the comparable data for a coal-S level of 4.4 daf wt % and an SCR in the gas cleaning configuration. By comparison, the measured SO₃ at S5 is inconsistent with the remainder of the tests with similar or lower coal-S that report much higher levels of SO₃ than this measured value of 10 ppm. We strongly suspect that the measured value is erroneously low. When the test results at S5 are omitted, the correlation coefficient (R) for the predicted SO₃

concentration at the different sampling locations is 0.97.

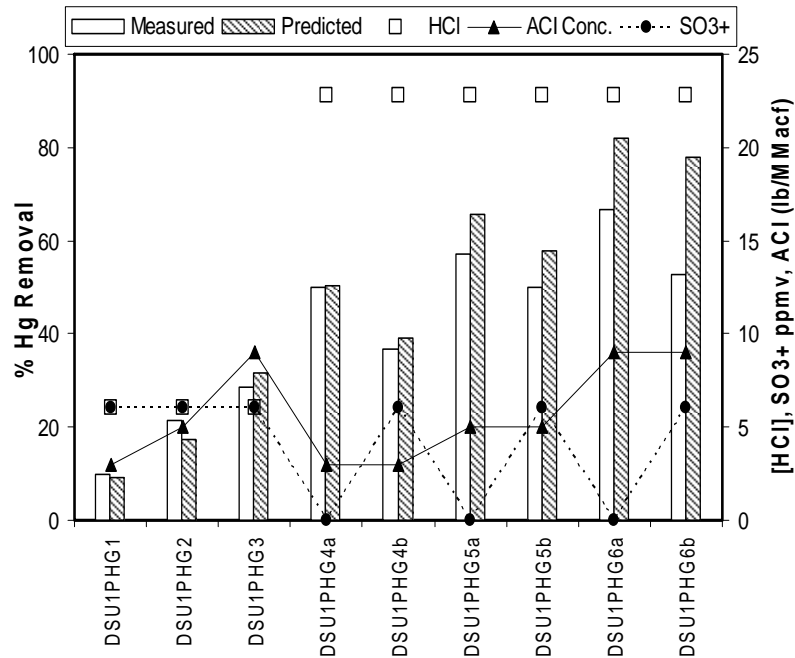
SO₃ Interference on Hg Capture By ACI

In full-scale gas cleaning systems it is almost never possible to standardize fuel quality throughout test campaigns as short as even several days, because coal-Cl variations are independent of all other coal properties. Gas cleaning conditions must also change to respond to variations in load and NO_x emissions, among many other factors. To contend with this inherent variability, we simulate each individual test based on the coal quality and gas cleaning conditions in effect while the Hg speciation data was recorded, to the extent possible. The following kinds of input data are required: The fuel properties consist of the proximate and ultimate analyses expanded with the Hg- and Cl-contents. A nominal flue gas composition is assigned with an equilibrium calculation from the fuel properties, fuel feedrate or furnace rating and load, and an economizer O₂ level. A continuous thermal history is constructed from the temperatures recorded at all Hg sampling locations; temperatures and transit times upstream of the measurement positions are almost always assigned from default specifications. UBC characteristics are assigned from LOI measurements and coal quality, and are also evaluated as a continuous function of residence time along the gas cleaning system. The flyash loading is determined by subtracting away the bottom ash, and expressed as a suspension loading in the whole flue gas. LOI is first used to estimate UBC, then added to the flyash loading. As the flue gas cools, the suspension loading and therefore the UBC surface area per unit volume increases continuously. Conversely, UBC and flyash are eliminated at the PCDs, according to specified collection efficiencies. Ammonia is injected at the residence time for the SCR inlet. Mercury sorbents are processed the same way. Hence, all the necessary gas cleaning conditions are specified as continuous functions of residence time along the entire gas cleaning system.

The sets of differential equations associated with the elementary reaction mechanisms are solved as one-dimensional initial value problems in transit time, beginning with the equilibrium flue gas composition at the furnace exit. Each simulation of a full-scale gas cleaning system takes several seconds on a mobile workstation operating at 2.9 GHz.

Daniel Unit 1 is a T-fired furnace with an ESP-only cleaning configuration. The plant fires a 60/40 or 80/20 blend of bituminous/subbituminous coals with the blends having average coal-Cl of approximately 100 and 430 daf ppmw, respectively. Only an average inherent LOI of 3.2 % was reported. Test-specific coal-Cl were not available for any of the ACI tests. The measured baseline Hg removal at this site was approximately 5 % when firing the 60/40 blend. No baseline removal for the 80/20 blend was reported. The calculated baseline SO₃ concentrations at Daniel were 7 and 9 ppmv, respectively, for 60/40 and 80/20 coal blends and no measured SO₃ concentrations were reported. Darco Hg was injected upstream of the ESP at concentrations of 3, 5 and 9 lb/MMacf. Tests at Daniel evaluated SO₃ interference on Darco Hg performance by addition of 6 ppmv SO₃ upstream of the ESP in all cases involving the 60/40 blend and in select cases involving the 80/20 blend. For the Darco Hg-LH (brominated activated carbon) tests, SO₃ was injected upstream of the ESP at a concentration of 6 ppmv in cases involving the 80/20

Figure 3. Comparison of measured and predicted Hg removals (%) for Darco Hg ACI tests at Daniel. SO₃+ represents additional SO₃ added to the baseline flue gas.



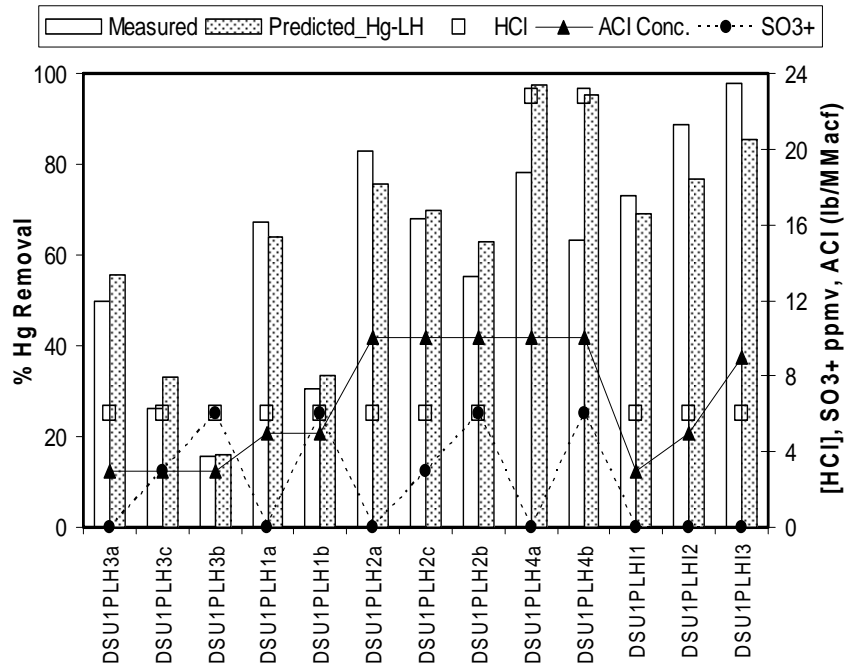
blend, and at 3 and 6 ppmv for the 60/40 blend. Hg speciation measurements were not reported for any of the ACI tests. The calculated acid dew point of approximately 137°C is greater than the temperatures across the ESP. The reported nominal temperatures at the ESP inlet and outlet were 137 and 121°C, and 141 and 130°C for the 60/40 and the 80/20 blends, respectively.

The measured and predicted Hg removals (as percentages of the total Hg inventories) for the Darco Hg cases are compared in Fig. 3. The tests labeled as DSU1PHG1–3 fired the 60/40 blend while the rest fired the 80/20 blend. The suffixes ‘a’ and ‘b’ in the 80/20 blend test labels (DSU1PHG4–6) represent 0 and 6 ppmv added SO₃, respectively. Six ppmv SO₃ was added in all three tests with the 60/40 blend (DSU1PHG1). For the Darco Hg-LH injection tests in Fig. 4, all tests fired the 60/40 blend except DSU1PLH4a–b, which fired the 80/20 blend. For several tests, the ACI injection location was shifted upstream to extend the residence time for Hg capture.

For the Darco Hg tests with the 60/40 blend (DSU1PHG1–3), the predicted Hg removals are within 5 % of the measured values. The measured Hg removals increased from 10 to 29 % while the predicted values increased from 9 to 32 % as the ACI concentrations were increased from 3 to 9 lb/MMacf. With no SO₃ interference, the simulated Hg removals would have increased from 28 to 38 % as the ACI concentration were increased from 3 to 9 lb/MMacf, which is 10–20 % greater than measured values.

For the Darco Hg tests involving the 80/20 blend (DSU1PHG4–6) with and without

Figure 4. Comparison of measured and predicted Hg removals (%) for brominated Darco Hg-LH ACI tests at Daniel. SO₃+ represents additional SO₃ added to the baseline flue gas.



added SO₃, the predicted Hg removals are within 10 % of the measured values for four of the six cases. The extent of inhibition of Hg capture by ACI due to SO₃ is accurately predicted at all ACI concentrations while the actual removals are over-predicted by at least 15 % for the highest ACI concentration of 9 lb/MMacf. Whereas the measured extents of SO₃ interference hardly change with ACI concentration in this range, the predictions show progressively less interference for increasing ACI concentrations.

For the cases involving brominated Darco Hg-LH in Fig. 4, the predictions are accurate for all cases except two tests involving the 80/20 blend (DSU1PLH4a–b). Although the predictions show the inhibitory effect of SO₃ for these tests, the predicted Hg removals are significantly greater than the measurements. This discrepancy can only be explained if the actual operating temperatures were lower than the nominal values by at least 10 degrees, which would promote stronger inhibition by SO₃. The predicted extents of Hg removal were within approximately 10 % of the measured values for all the remaining tests. The simulations accurately predict the extent of inhibition of SO₃ on Hg capture by Darco Hg-LH at all three ACI concentrations and three added SO₃ concentrations for the 60/40 blend. Hg removals at tests DSU1PLHI1–3, where the sorbent injection location was shifted upstream, are also predicted within 15 % by accounting for the additional sorbent residence time in the flue gas in the simulations.

At comparable flue gas conditions, the brominated Darco Hg-LH removed 6, 9 and 27 %

more Hg than the untreated Darco Hg at injection concentrations of 3, 5 and 9 lb/MMacf, respectively, in the presence of 6 ppmv added SO₃. The predictions at Daniel clearly show the accuracy of the mechanisms to predict SO₃ inhibition of Hg capture by ACI because the predictions are within 10 % of the measurements for seven of the nine tests involving Darco Hg and for nine of the thirteen involving Darco Hg-LH. The correlation coefficient for the predicted removals for all tests at Daniel except two Darco Hg-LH tests with the 80/20 blend was 0.93 with a std. dev. of 8.7 % of the Hg inventory, which is well within the measurement uncertainties.

DISCUSSION

The proposed SO₃ production mechanism was validated against a literature database comprising the full range of coal-S, furnace stoichiometry, and cleaning conditions in commercial power plants. With the exception of one abnormally low test measurement, the correlation coefficient for the predicted SO₃ concentration at different sampling locations for fourteen full-scale plants is 0.97. Homogeneous oxidation along the convective passes and heterogeneous oxidation along SCR catalysts determine SO₃ concentrations into the APH, but heterogeneous oxidation on flyash is almost always unimportant.

Once the SO₃ production mechanism was integrated into our validated mechanisms for Hg transformations, the simulations correctly identified which sites in the Ph. II NETL Hg field-testing database were afflicted by SO₃ interference, and predicted its impact on Hg removals. Simulations accurately predicted the effect of SO₃ on Hg removal by both conventional and brominated activated carbons at Daniel. The predicted removals at this site for the different coal blends, activated carbons and SO₃ injection concentrations were within 15 % of the measured values for 19 of the 22 test measurements. The proposed mechanisms clearly identify whether interference by SO₃ is important or not. The proposed SO₃ interference mechanism has also been validated with additional data from a slipstream test facility¹¹.

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