ELECTRIC POWER
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Estimating Total Sulfuric Acid Emissions from Stationary Power Plants

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PRODUCT DESCRIPTION

This report provides a methodology to estimate sulfuric acid emissions from fossil-fuel-fired electrical power production facilities. The methodology was developed by Southern Company Services (SCS) and modified by EPRI with permission from the developers. The calculations presented in this report allow owners of power plants to estimate the sulfuric acid manufactured during fuel combustion, removed by air pollution control equipment or flue gas treatment, and released to the environment in stack gases.

Results and Findings

The power generation units considered in the report include coal- and oil-fired steam generating units as well as simple-cycle and combined-cycle natural gas- and oil-fired combustion turbines. Calculation procedures are provided for estimating removal or production of sulfuric acid by pollution control devices and flue gas treatments.

Challenges and Objectives

Sulfuric acid releases from electric power generating units must be reported to EPA on an annual basis if the amounts manufactured, processed, or otherwise used exceed the limits set by the EPA's Toxics Release Inventory (TRI) program.

Applications, Value, and Use

This report will be useful to environmental staff of power generation facilities responsible for TRI reporting.

EPRI Perspective

The methodology presented in this report is used by many power generation facility owners to estimate sulfuric acid emissions. There is currently no other published approach with a comparable amount of supporting measurements. EPRI will continue to enhance the methodology by adding to the underlying database and refining the calculations to address new flue gas treatment approaches.

Approach

The manufacture and release of sulfuric acid from coal-, oil-, and natural gas-fired electrical generation units were estimated from field test data. Measurements from multiple facilities were used to develop sulfuric acid removal factors for various coal types and facility configurations.

Keywords

Sulfuric acid
Toxics Release Inventory
Air emissions

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The methodology described in this document was developed by Southern Company Services and modified, with permission, by EPRI. Individuals responsible for the development of the original Southern Company sulfuric acid model are Keith E. Harrison and Larry S. Monroe, Ph.D. of the Southern Company.

EXECUTIVE SUMMARY

The U. S. Environmental Protection Agency's (EPA's) Toxic Release Inventory (TRI) reporting system requires that, beginning in 1998, electric utilities estimate their emissions of over 600 chemicals. Sulfuric acid (H_2SO_4) is one of the chemicals included in the TRI reporting requirement, when it is present in an aerosol form. The EPA defines sulfuric acid aerosols as "includ[ing] mists, vapors, gas, fog, and other airborne forms of any particle size." Sulfuric acid aerosol is formed during combustion of fossil fuels when sulfur trioxide (SO_3) in hot combustion gases combines with water to form sulfuric acid, and then cools and condenses to form small droplets of the acid.

This document provides a methodology to estimate sulfuric acid emissions from fossil-fuel-fired electrical power production facilities. The methodology described in this report was developed by Southern Company Services (SCS). Between 2000 and 2005, SCS developed several versions of the estimation methodology and released draft reports on request. The SCS model is widely used in the electrical power generation industry for TRI reporting and other emissions estimation purposes. In 2007, EPRI received permission from Southern Company Services to modify the SCS estimation method to include additional data and improvements, and to publish this method under EPRI sponsorship. The current 2010 version of this report contains several updates and changes to EPRI's 2008 version (Report No. 1016384).

The basic method for estimating sulfuric acid emissions remains unchanged from that described by SCS (2005). First, the method estimates manufacture of SO_3 and sulfuric acid from three sources: (1) combustion of fuel, (2) the NOx control process selective catalytic reduction (SCR), and (3) flue gas conditioning (FGC), in which SO_3 is added to flue gas to improve particulate control device performance. Next, the actual release of SO_3 or H_2SO_4 is calculated by adjusting the manufacturing estimate to account for processes known to remove SO_3 and H_2SO_4. These include a byproduct reaction of SCR, as well as the NOx control process of selective non-catalytic reduction (SNCR), and other types of FGC. This paper also provides a method to account for the impact of SO_3/H_2SO_4 removal technologies such as the addition of calcium-based, sodium-based, or other alkaline reagents, as described by Dombrowski (2004) and Weilert (2004).

The current estimation method is based on an ever-growing database of measurements of SO_3 emissions from combustion systems, primarily coal-fired boilers. The 2008 version of the model was based on data from over 40 coal-fired units, and the current 2010 version adds data from 13 new sources, representing various boiler types and coal sources. The estimates of SO_3 production from combustion of coal are consistent with theoretical predictions that approximately 1% of the sulfur in coal is converted to SO_3, although a wide range of conversions from 0.2% to 1.6% is reported, depending on coal source and boiler type. Data are obtained from field tests, reporting the removal of SO_3 or H_2SO_4 by air heaters, particulate control equipment such as electrostatic precipitators (ESPs) and fabric filters, and SO_2 control equipment. The removal data are used to develop "technology factors" that represent the amount of sulfuric acid that passes through, but is not captured by, each pollution control device. The technology factors are used to estimate quantities released to the air.

The 2010 version adds more than 10 new sources of measurement data of SO_3 emissions and introduces a new methodology for determining a Fuel Impact Factor (estimate of SO_2 conversion to SO_3 in the boiler) for eastern bituminous coals. Several “technology factors”, used in the model to reflect sulfuric acid removal by pollution control devices, have been updated with new and re-evaluated measurement data.

As with all estimation procedures, the methodology described in this report and the factors developed from the available data will not be applicable to every facility configuration or fuel type. Site-specific measurements of SO_3 or H_2SO_4 emissions from a power facility, if available, should always be used in place of the estimates derived with this method.

CONTENTS

1
INTRODUCTION

Background

Estimation of sulfuric acid emissions from power plants is a topic of increasing importance to the U.S. electric utility industry. Most significantly, Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA), also known as the Toxic Release Inventory (TRI), requires facilities that “manufacture,” “process,” or “otherwise use” a listed chemical above certain threshold amounts to report their annual releases of the chemical to EPA and state agencies. For sulfuric acid, the TRI reporting requirements are triggered if a facility “manufactures” or “processes” more than 25,000 pounds of this chemical or “otherwise uses” more than 10,000 pounds of it in a given calendar year.

Sulfuric acid is a listed TRI chemical. In June 1995, the U. S. Environmental Protection Agency (EPA) modified the list of chemicals subject to the EPCRA § 313 reporting requirements so that only aerosol forms of sulfuric acid would be subject to the TRI reporting requirements (EPA, 1995a). EPA defines sulfuric acid aerosols as “includ[ing] mists, vapors, gas, fog, and other airborne forms of any particle size.” Although initially it appeared that only liquid droplets of sulfuric acid needed to be reported, the present method estimates the sulfuric acid emissions regardless of the physical state of the molecules.

Beginning on July 1, 1999, certain coal- and oil-fired electric power plants have been required to report annual releases of TRI chemicals that they manufacture, process or otherwise use above threshold amounts. Under EPA’s EPCRA § 313 regulations, coal- and oil-fired electric utilities are deemed to “manufacture” sulfuric acid. Thus, electric utilities have to submit TRI reports on sulfuric acid releases if they “manufacture” more than 25,000 pounds of the chemical in a given reporting year (EPA, 1997).

Emissions of sulfuric acid have received considerable attention in recent years with the broad application of selective catalytic reduction (SCR) NOx control technology. The use of SCR unavoidably contributes to production of sulfur trioxide (SO_3), the precursor of sulfuric acid. Several notable incidents have been witnessed where an increase in sulfuric acid emissions, as manifested by an increase in stack plume visibility, was attributed to the addition of SCR process equipment to an existing power plant. The deployment of approximately 115 GW of selective catalytic reduction (SCR) from 1997 through 2009 has prompted power plant owners to conduct extensive measurements documenting the fate of SO_3 and sulfuric acid in power plants.

The methodology described in this report was developed by Southern Company Services (SCS). Between 2000 and 2005, SCS developed several versions of the estimation methodology and released draft reports informally (Hardman, 1998; Hardman, 1999; Monroe, 2001, Harrison, 2004, and Harrison, 2005). The SCS model is widely used in the electrical power generation industry for TRI reporting and other emissions estimation purposes. In 2007, EPRI received permission from Southern Company Services to modify the SCS estimation method to include additional data and improvements, and to publish this method under EPRI sponsorship. The 2008 version of the model added the ability to estimate emissions based on a specified sulfuric acid flue gas concentration at the stack. This approach can be used when alkali injection is employed to reduce sulfuric acid emissions.

The current methodology is largely unchanged from the previous version of this model (EPRI, 2008), making use of correlation factors that relate coal type and power plant configuration to sulfuric acid emissions. The current version updates several of the “technology factors” (F2 factors, used to reflect the impact of pollution control devices) with new SO_3 measurements. The current version contains a modified methodology to determine a Fuel Impact Factor (F1 factor, used to reflect the impact of coal type on conversion of SO_2 to SO_3 in the boiler) for eastern bituminous coals. Rather than presenting different F1 factors for low-sulfur and high-sulfur eastern bituminous coals, the model now represents the F1 factor as a linear relationship between boiler SO_2 and the rate of conversion to SO_3. The current report also corrects an error in a conversion factor for calculations of sulfuric acid releases during alkali injection, as documented in an errata sheet issued in April, 2009 (EPRI, 2008).

Objective

The objective of this report is to present a methodology for estimating sulfuric acid emissions from power generating facilities, for use in Toxics Release Inventory reporting and other applications. The scope of units considered includes coal- and oil-fired steam generating units, as well as simple cycle and combined cycle natural gas- and oil-fired combustion turbines. To date, the most authoritative and documented data describe sulfuric acid emissions from coal-fired steam generators. The focus on this category of units is due to the increased availability of measurements describing the fate of sulfuric acid attributable to the retrofit of SCR process equipment on coal-fired steam generators.

Report Organization

Section 2 of this report addresses the uncertainty in measuring SO_3 concentration using the preferred controlled condensation system (CCS) method, and the accuracy and representativeness of the available data. Section 3 outlines the general methodology adopted in this model while Section 4 describes the details of the methodology, focusing on data that can be used to predict sulfuric acid manufacture by combustion. This section also summarizes data describing the removal of sulfuric acid across air heaters, ESPs, and wet flue gas desulfurization (FGD) process equipment. Section 5 outlines how to conduct the calculation for steam boilers firing a mixture of fuels. Section 6 addresses simple cycle and combined cycle combustion turbine applications. Example calculations for various power plant configurations are presented in Appendix A. A chronology of changes to the EPRI sulfuric acid model is presented in Appendix B.

2

MEASUREMENT UNCERTAINTY

A predictive method for sulfuric acid emissions requires knowledge of sulfuric acid production and the fate of emissions from specific boilers and combustion turbines, to an acceptable degree of measurement accuracy. In addition, a large database of measurements from many electric generating units (EGUs) is desired to obtain a robust predictive method. Both the size and the representativeness of the measurement database are critical to the accuracy of a predictive method.

The predictive correlations presented in this report are based on data obtained from field tests conducted predominantly within the last 10 years, with some estimates conducted in the1990s. The quality of the data is thought to vary widely. It was not possible to obtain quality control information for all of the available measurements; thus, it was not possible to critically review all data used in this model.

The technique used to measure SO_3/H_2SO_4 is not known for all data sources, but most measurements were conducted using the controlled condensate system (CCS), a widely used technique that is generally considered the most accurate method for measuring SO_3/H_2SO_4 in stack gases from stationary combustion sources. EPA Method 8 is sometimes used for this purpose, but that method has a known positive bias from oxidation of SO_2 to SO_3 in the impinger solution.

CCS Measurement Uncertainty

A series of field and laboratory trials conducted by EPRI evaluated the measurement bias of the CCS technique by comparing results from both laboratory tests and field trials (EPRI, 2001). SO_3/H_2SO_4 measurements at similar gas compositions were compared in a 1) clean, ash-free laboratory environment; 2) simulated ash environment, and 3) actual field duty. The findings of the EPRI tests conducted under high-ash conditions are applicable to much of the field data used to derive removal factors in the current estimation model. The results showed that, when fly ash was present in the flue gas stream, the technique imposed a low bias (e.g., indicated lower SO_3/H_2SO_4 than measured in the ash-free laboratory environment), due to reactions of SO_3 or sulfuric acid with fly ash in the filter thimble holder upstream of the CCS condenser. Conversely, the EPRI tests indicated that use of CCS downstream of the particulate control device produces unbiased measurements, as long as appropriate procedures are followed.

The extent of bias observed in the EPRI study depended on the sampling location, which could be the air heater inlet, air heater outlet, or flue gas desulfurization outlet. Furthermore, the bias depended on the quantity of ash collected, the alkalinity of the ash, and the coal sulfur content (e.g., SO_2 content in the sample gas). Measurement bias in the simulated ash environment was observed for both high sulfur coal and low sulfur Powder River Basin (PRB) coal; however biasing in the PRB coal tests can generally be considered non-significant in light of already low SO_3 concentrations and the expected absorption of sulfuric acid with the alkaline ash in actual field tests. Data for high sulfur coal suggested a low bias of 20-25% could occur in measurement locations upstream of a particulate control device with typical ash loadings, and no significant bias downstream of the particulate control device.

The precision of the CCS data used in this estimation model can be estimated from the variability among duplicate measurements believed to be conducted under the same process conditions. Data from recent field trials with experienced test crews suggest a precision of up to ± 20% is realistic for most conditions. The repeatability of the CCS measurements depends on avoiding stratification within the gas stream (traversing is very difficult), maintaining correct temperatures in the sampling train, and having well trained sampling personnel. Therefore, the precision of the entire data set used in this model, which includes data from older studies of unknown quality, is expected to be closer to ± 50%.

Representativeness

The accuracy of the correlations presented in this report depends on the representativeness of the constituent data points. For some power plant configurations, only a few measurements are available, and the correlations provide only rough approximations of the flue gas SO_3/H_2SO_4 releases for similar units. The category with the largest number of data points is dry-bottom boilers, firing low sulfur, eastern bituminous coal. In general, the number of SO_3 measurements for various power plant configurations are proportional to the occurrence of those configurations among the total population of U.S. EGUs. The number of measurements in each power plant category should be considered when applying this model; factors based on one measurement have much higher uncertainty than factors based on dozens of measurements.

As a consequence of the uncertainty in SO_3/H_2SO_4 measurements and the limited number of data points that comprise the relevant correlations, the predictive technique should be assumed to provide estimates within a ± 50% relative accuracy.

3

BACKGROUND AND METHODOLOGY OVERVIEW

This section provides a brief overview of sulfuric acid production mechanisms in power plants and presents the basic equations for estimating sulfuric acid releases. A detailed review of this topic has been provided by Srivastava (2004) and more recently by Monroe (2006).

The production or manufacture of SO_3, and ultimately sulfuric acid, is determined initially by processes occurring directly within the flame zone of a boiler, the convective heat transfer sections, or environmental control components. These production or manufacturing processes can be gas phase or can be induced by catalysis on the surface of fly ash particles or heat removal surfaces.

Mechanisms that remove sulfuric acid from the flue gas also can occur both in the gas phase and on heat transfer surfaces, usually promoted by ash-derived deposits. The amount of sulfuric acid released from the stack is the aggregate result of production mechanisms, generally occurring at temperatures above 650°F, and removal mechanisms, including alkali-based sorbent injection, occurring at lower temperatures.

Factors Affecting Manufacture and Release

The method estimates the manufacture and the subsequent release of sulfuric acid from the power generation process. The ***manufacture*** of sulfuric acid is defined as any process step that increases the flue gas content of sulfuric acid, regardless of its ultimate fate. To estimate the ***release*** of sulfuric acid, the manufacture estimate is corrected by a factor or series of factors to account for sulfuric acid removal within the system.

Three process steps ultimately lead to the manufacture of sulfuric acid in a fossil fuel-fired electricity generation unit: the combustion process, selective catalytic reduction (SCR) for NOx control, and flue gas conditioning. All remaining steps in the power generation process reduce sulfuric acid. Therefore, the total sulfuric acid released is the cumulative sum of that manufactured, adjusted by sulfuric acid losses.

The manufacture of SO_3, the precursor to sulfuric acid, is calculated in this model as shown in Equation 3-1.

Equation 3-1 $$\mathbf{TSAM = EM_{Comb} + EM_{SCR} + E_{FGC}}$$

where,

$TSAM =$ Total manufacture of sulfuric acid

$EM_{Comb} =$ Manufacture of sulfuric acid through combustion

$EM_{SCR} =$ Manufacture of sulfuric acid from SCR

$EM_{SCR} =$ Manufacture of sulfuric acid from FGC

The Total Sulfuric Acid Release (TSAR) from a combustion unit equipped with SCR/SNCR NOx control and FGC is represented by Equation 3-2.

Equation 3-2 $$\mathbf{TSAR = ER_{Comb} + ER_{SCR/SNCR} + ER_{FGC}}$$

where,

TSAR = Total release of sulfuric acid

ER_{Comb} = Sulfuric acid released through combustion

$ER_{SCR/SNCR}$ = Sulfuric acid released from SCR (or SNCR)

ER_{FGC} = Sulfuric acid released from FGC

Combustion Process

Manufacture

A detailed analytical study by Senior (2002) explored details of SO_2 oxidation to SO_3. Specifically, the author modeled the relevant reaction sets employing the temperature-time history of a typical utility boiler, considering gas phase events only and ignoring catalytic effects. The results showed that insignificant SO_3 formed in the early stage of the flame, but SO_3 production increased as the gases exited the flame zone and cooled. The author reported production of SO_3 to be essentially complete prior to flue gas entering the economizer section. The observation that most SO_3 forms during cooling from post-flame temperatures (2,900-3,100°F) to temperatures typical of the economizer entrance was also noted by Buckley (2002). Senior further quantified the relationship between coal sulfur content, excess air, and SO_3 production that has been empirically observed by previous investigators. Specifically, the results showed that after four seconds of residence time, SO_3 production could range from between 0.3 - 0.6% of the flue gas SO_2 concentration.

In the absence of SCR NOx control or FGC, the boiler or turbine combustion process comprises the only source of sulfuric acid. The sulfuric acid manufacture by the combustion process (EM_{Comb}) is expressed as follows:

Equation 3-3 $$\mathbf{EM_{Comb} = K \bullet F1 \cdot E2}$$

Where K is a constant, F1 is the Fuel Impact Factor describing the SO_3 production associated with combustion for a specific fuel type, and E2 is the annual rate of SO_2 production. Further details of this relationship and the derivation of constants and other terms are presented in Section 4.

Release

The release of sulfuric acid attributable to the combustion process is determined by adjusting the manufactured SO_3 by the removals in the following equipment: the air heater, electrostatic precipitator (ESP) or other particulate control device (PCD), and flue gas desulfurization (FGD) equipment. The release of sulfuric acid is calculated by applying Technology Impact Factors

(F2) that describe the fraction of sulfuric acid that penetrates each downstream equipment component. The sulfuric acid released by combustion (ER_{Comb}) is described by the following:

Equation 3-4 $$ER_{Comb} = EM_{Comb} \bullet F2 \text{ (all that apply)}$$

The development of Technology Impact Factors (F2) for each downstream component is addressed in Section 4.

SCR/SNCR NOx Control

Manufacture

The SCR process increases the production of SO_3, and therefore, H_2SO_4, as a percentage of SO_2. SO_3 production can range from as low as 0.3%, for the most recent catalyst technology, to as high as 3% of the SO_2 concentration.

The production of SO_3 from SO_2 is a well-known consequence of SCR, and the degree of SO_2 oxidation is a performance variable that should be part of catalyst procurement specifications. To a degree, SO_3 production can be mitigated by reducing the content of vanadium pentoxide and compensating with other catalyst oxides such as tungsten or molybdenum, which offer improved selectivity (e.g., lower SO_2 oxidation) but also lower activity for NOx removal. Alternatively, advanced catalyst formulations can be used that concentrate the vanadium-containing active ingredients on the catalyst surface and minimize content within the substrate, lowering SO_2 oxidation. To achieve an equivalent level of NOx and residual ammonia slip, a low SO_2 oxidation catalyst may require a larger volume of catalyst than one for which SO_2 conversion is not constrained. In general, the degree of SO_2 oxidation ranges from about 0.2% to 1.5% for most SCR process reactors designed for bituminous coals. If SCR is applied to extremely low sulfur, high alkalinity coals such as PRB, higher SO_2 oxidation is acceptable. Depending on how the measurement of SO_2 oxidation is performed, the oxidation can be 3% or higher.

In many instances, owners and catalyst suppliers prefer that measurements to quantify SO_2 oxidation for the purpose of commercial guarantees be conducted not with authentic flue gas but in a laboratory-scale test facility, without fly ash present. This approach has the advantage of improved accuracy and repeatability of the SO_3 concentration. The measurements are generally conducted using CCS. However, particularly for PRB coals, this method will over-predict SO_3 manufactured by the SCR, as the mitigating role of high fly ash alkalinity is not considered. Consequently, the role of fly ash alkalinity must be considered in predicting SO_3 manufactured by SCR.

The observation that calculated laboratory-scale SO_3 values at the exit of an SCR reactor exceed measurements in the field has been witnessed on numerous occasions. Specifically, Lindenhoff (2004) reported that the measured SO_2 oxidation rate for PRB-generated flue gas of 1.25% was below the 1.6% value predicted based on the boiler and SCR catalyst specifications. Further, tests conducted by this catalyst manufacturer noted significant absorption of SO_3 generated within the SCR reactor prior to the air heater. Sufficient data was accumulated to derive both a mathematical model and to project a graphical relationship describing SO_3 removal within an SCR reactor as a function of both ash content and the number of alkaline sites available in the flue gas stream.

An alternative NOx control process, selective non-catalytic reduction (SNCR), does not use a catalyst and does not promote the oxidation of SO_2 to SO_3. Accordingly, there is no manufacture of sulfuric acid attributable to SNCR.

The following relationship describes the total H_2SO_4 manufactured from an SCR equipped utility boiler or steam generator:

Equation 3-5 $$EM_{SCR} = K \bullet S2 \bullet f_{sops} \bullet E2 \bullet F3_{SCR}$$

Where K is a constant, S2 is the catalyst SO_2 oxidation rate, f_{sops} is the fraction of the year in which flue gas is directed through the SCR, E2 is the annual rate of SO_2 production, and $F3_{SCR}$ is the Technology Impact Factor for SCR used to adjust for the presence of alkaline fly ash. Further details of this relationship and the derivation of constants and other terms are presented in Section 4.

Release

Both SCR and SNCR can introduce residual ammonia (NH_3), also called ammonia slip, into the flue gas. This residual ammonia can react with SO_3 or sulfuric acid to form ammonium sulfate and/or ammonium bisulfate, thereby removing from the flue gas some of the SO_3 that is a precursor to sulfuric acid, and reducing the amount released.

For an SCR, ammonia slip is expected to usually range between 0 and 2 parts per million (ppm) for bituminous coal cases. Higher values of ammonia slip are possible if the unit has not been recently tuned, the boiler or SCR process operates under upset, or as the catalyst ages. Higher ammonia slip may be tolerable in PRB coal applications, since ammonia is not readily absorbed by the highly alkaline PRB ash and adverse operational impacts (air preheater pluggage and ash contamination by ammonia) are avoided. Reactions between the residual ammonia and SO_3 or H_2SO_4 occur in the air preheater and result in a solid product that may deposit or accumulate on the surface of the fly ash. Any SO_3 or H_2SO_4 that participates in these reactions is no longer chemically present as sulfuric acid and is not required to be reported to the EPA TRI program as a release of sulfuric acid.

SNCR employs ammonia or urea injection in the upper furnace for NOx reduction. The higher temperatures characteristic of the upper furnace zone (1,800 to 2,400°F, as compared to 700°F for SCR) do not require reduction catalyst so there is no additional manufacture of SO_3 or sulfuric acid. Typically, SNCR systems operate with higher levels of residual ammonia (5 to 10 ppm), so any sulfuric acid that is present from combustion is reduced through reaction with the ammonia. Consequently, SNCR systems will always *reduce* the overall amount of sulfuric acid released, while SCR systems can *reduce* but will likely *increase* the amount of sulfuric acid released.

The reactions between SO_3 and/or H_2SO_4 and ammonia produce ammonium sulfate [$(NH_4)_2SO_4$] and/or ammonium bisulfate (NH_4HSO_4). While both chemicals are solids, the bisulfate pairs one molecule of ammonia with one of sulfuric acid, while the sulfate requires two ammonia molecules for each sulfuric acid. Which reaction product is present is usually determined by the stoichiometry, or the relative amount of each substance on a mole basis, that is present in the flue gas. When ammonia is present in an amount over twice the mole content of the sulfuric acid, the reaction product will always be the ammonium sulfate. Conversely, when sulfuric acid is present in an amount on a mole basis greater than ammonia, the product will be ammonium bisulfate. Between these two extremes, a mixture of ammonium sulfate and bisulfate is produced.

An SCR-equipped unit firing bituminous coals with low-to-medium sulfur content will always produce an excess of sulfuric acid over ammonia slip. Accordingly, ammonium bisulfate is the primary byproduct anticipated. For subbituminous, PRB, and lignite coals, any sulfuric acid produced is typically adsorbed by the ash and it is likely that residual ammonia will exceed sulfuric acid content on a mole basis. Under these conditions, ammonium sulfate is the likely product.

For SNCR-equipped units, ammonia slip levels of 5 ppm and possibly higher will favor ammonium sulfate, particularly for western U.S. coals where the alkaline fly ash will reduce the SO_3 content. For eastern bituminous coals, which have generally higher sulfur content and lower ash alkalinity, ammonium bisulfate will likely predominate.

For the purpose of predicting sulfuric acid emissions, these distinctions are not important. A single molecule of sulfuric acid will capture a single molecule of ammonia, producing ammonium bisulfate. If additional ammonia is available, the ammonium bisulfate can react with another ammonia molecule to form ammonium sulfate. It can be assumed that all sulfuric acid forms ammonium bisulfate before any further reaction to the ammonium sulfate form occurs. This assumption leads to the calculation strategy that ammonia captures all of the sulfuric acid it can as ammonium bisulfate, and since the bisulfate form is no longer reportable, the sulfuric acid disappears from the release calculation. Additional ammonia reacting with the ammonium bisulfate is of no consequence to the sulfuric acid calculation – although this issue will be important when estimating ammonia releases.

The sulfuric acid released from SCR or SNCR is determined by subtracting from the sulfuric acid manufactured the amount removed by the residual ammonia, or ammonia slip. For SCR, the sulfuric acid released (ER_{SCR}) is estimated with the following relationship:

Equation 3-6 $$\mathbf{ER_{SCR} = [EM_{SCR} - (K_s \bullet B \bullet f_{sreagent} \bullet S_{NH3})] \bullet F2_x}$$

Where K_S is a constant, B is the coal burn in TBtu/yr, $f_{sreagent}$ is the fraction of SCR operation with reagent injection, S_{NH3} is the NH_3 slip for the SCR/SCNR and F2 are any applicable downstream, Technology Impact Factors. These calculations and factors are described further in Section 4.

For SNCR, as there is no sulfuric acid manufacture term, the sulfuric acid release estimate (ER_{SNCR}) is a negative term which, when included in the calculations, will result in an overall reduction of sulfuric acid emissions.

Flue Gas Conditioning

Manufacture

Flue gas conditioning (FGC) is a process that is typically used in power plants to assist in particulate control in an ESP or baghouse. The conditioning additives can be any of the following: SO_3, SO_3 plus NH_3, or NH_3 alone. In SO_3-based FGC, SO_3 is introduced into the flue gas either preceding or following the air heater. The SO_3 is typically produced on-site from sulfurous fuel that is burned to produce SO_2, which is then catalytically oxidized to SO_3 with a conversion rate typically exceeding 95%. When injected into the flue gas, the SO_3 immediately reacts with water vapor to create sulfuric acid, thus resulting in the manufacture of sulfuric acid. Estimating the manufacture source requires knowledge of the concentration of SO_3 injected and the associated oxygen content of the flue gas.

Equation 3-7 presents an equation to estimate the manufacture of sulfuric acid from this source, where K_e is a constant, B is the coal burn, f_e is the FGC operating factor, and $I_s$is the SO_3 injection rate. Further details and derivation of the constant are provided in Section 4.

Equation 3-7 $$\mathbf{EM_{FGC} = K_e \bullet B \bullet f_e \bullet I_s}$$

Release

The release of sulfuric acid attributable to FGC requires adjusting for the reaction with NH_3 that may be introduced as part of a flue gas conditioning scheme, either with or without sulfuric acid. Analogous to the case of SCR and SNCR, the concentration of NH_3 and the associated O_2 content of the flue gas must be estimated. Accordingly, FGC can manufacture sulfuric acid, but can also remove sulfuric acid if NH_3 is injected alone or in quantities greater than the sulfuric acid. The following equation describes the relationship to determine the release of sulfuric acid attributed to FGC.

Equation 3-8 $$\mathbf{ER_{FGC} = [EM_{FGC} - (K_e \bullet B \bullet f_e \bullet I_{NH3})] \bullet F3_{FGC} \bullet F2}$$

Where $F3_{FGC}$ is the Technology Impact Factor for FGC, used to adjust the releases based on the injection point of SO_3. The Technology Impact Factors (F2) describe the fraction of sulfuric acid that penetrates the air heater (for FGC that is introduced ahead of the air heater), and for the particulate control device and FGD (for FGC that is introduced after the air heater). The basis for the F2 factors and the detailed equations for quantifying the manufacture and release of sulfuric acid are presented in Section 4.

Alkali Injection

Many utility operators inject alkali into the flue gas to control SO_3. A wide variety of alkali materials based on calcium, sodium, or in some cases magnesium compounds, have been used with varying degrees of effectiveness to remove SO_3. These alkali materials include sodium bisulfate, trona, and various types of lime (conventional, hydrated, and magnesium enhanced).

Sodium bisulfate (SBS) is the most widely used reagent for control of SO_3. SBS is introduced into the flue gas, usually at the air heater exit, but in some units at the air heater inlet, to maximize residence time and improve SO_3 removal. SBS can be highly effective in removing SO_3. Additional sodium can be added to the flue gas to compensate for any compromise in ESP performance due to increased ash resistivity associated with SO_3 reduction. A detailed summary of experience with the SBS concept has recently been published (Moser, 2007).

Trona is another sodium-containing reagent that is used to control SO_3. Trona can be injected at several locations within the boiler, but most applications introduce trona at the air heater exit, prior to the particulate collector (Ritzenthaler, 2006). As with SBS, additional sodium introduced into flue gas is advantageous to compensate for the reduction in ESP performance.

Several forms of calcium-based sorbents can be utilized. These are injected at various locations in the flue gas, including the economizer inlet, economizer outlet (e.g., air heater inlet), and the air heater outlet. A survey of recent experience with lime-derived sorbents addressed the advantages of this approach (Benson, 2006a). Hydrated lime has been shown to be an effective calcium-based reagent for SO_3 control (Gale, 2006), as has lime supplemented with magnesium hydroxide (Benson, 2006b). Calcium–based sorbents can be very effective in reducing SO_3, but may compromise ESP performance, as the reduced SO_3 content in flue gas increases the electrical resistivity of the ash on the collecting plate. For this reason, some operators have proposed using both calcium- and sodium-based sorbents, the latter to both augment SO_3 removal and promote ESP performance.

In summary, any of several alkali materials can be used to control SO_3, with the least cost solution depending on the plant and access to low cost sorbent.

Plant units that deploy alkali injection will have conducted field tests to determine the resulting SO_3 concentration in flue gas. In most cases, the tests will be conducted at the stack. The alkali injection system usually is operated to reduce SO_3 emissions to between 5 and 15 ppm, an optimal range to prevent formation of a visible plume.

In the 2008 version of the Sulfuric Acid Model, EPRI added a procedure to estimate SO_3 stack releases from EGUs that employ alkali injection for SO_3 control, using as an input to the model the measured or estimated stack gas SO_3 concentration. A procedure to convert measured sulfuric acid concentration in flue gas to a mass emission rate is summarized below and described in more detail in Section 4. An example application of this method is provided in Appendix A.

Equation 3-9 $$ER_{ALKINJ} = K_{alkali} \bullet B \bullet S_{SO3} \bullet F2_x \bullet F_{alkali}$$

Where K_{alkali} is a constant, B is the coal burn, S_{SO3} is the measured SO_3 content with injection, F_{alkali} is the fraction of time alkali injection is in operation, and F2 are any applicable downstream Technology Impact Factors.

To estimate SO_3 <u>manufacture</u> with alkali injection, plant owners should use the standard approaches given in Section 4 for the appropriate plant configuration. At this time, EPRI does not have sufficient information to estimate the impact on SO_3 formation of adding alkali at various points in the fuel combustion and stack gas treatment process. Assuming that there is no reduction of SO_3 formation is conservative for a <u>threshold</u> determination for TRI reporting purposes.

Users of this approach should be cautioned that the current EPA-approved test method for SO_3 (Method 8) has a significant positive bias, and that corrections for this bias may be needed to accurately assess flue gas concentrations. A more accurate method is the controlled condensate system, although this method is not currently approved by EPA for this purpose.

4

ESTIMATING GUIDELINE: STEAM BOILERS

This section describes an estimation procedure for calculating the manufacture and release of sulfuric acid from coal-fired steam generators. The topics addressed are (a) formation within the furnace; (b) the role of SCR, (c) flue gas conditioning (FGC), and (d) alkali injection; and (e) the removal by downstream equipment such as air heaters, ESPs or other particulate control devices, and FGD process equipment. Each of the subsequent sections in this chapter provides the information to conduct this stepwise calculation.

Manufacture and Release from Combustion

The premise of the methodology is that the amount of sulfuric acid manufactured by the boiler is a function of the amount of SO_2 released – determined either from coal usage (amount burned and sulfur content) or from continuous emission monitoring system (CEMS) output. Units equipped with FGD equipment or other methods of SO_2 control are required to use either coal data or CEMS measurements from ahead of the scrubber. As described below, it may be necessary to correct CEMS SO_2 data for non-ideal stack flow conditions.

Sulfuric Acid Manufactured by Combustion (EM_{Comb})

The following relationship is proposed to estimate the sulfuric acid *manufactured* from combustion in utility sources:

Equation 4-1 $EM_{Comb} = K \bullet F1 \bullet E2$

where,

EM_{Comb}= total H_2SO_4 *manufactured* from combustion, lbs/yr

K = Molecular weight and units conversion constant
= 98.07 / 64.04 • 2000 = 3,063

98.07 = Molecular weight of H_2SO_4

64.04 = Molecular weight of SO_2

Conversion from tons per year to pounds per year – multiply by 2000.

F1 = Fuel Impact Factor

E2 = Sulfur dioxide (SO_2) emissions, either: (1) recorded by a continuous emissions monitor, tons/yr, or (2) calculated from coal burn data, tons/yr.

The Fuel Impact Factor (F1) is a numerical value or a mathematical relationship reflecting the conversion of SO_2 to SO_3 in the boiler for a specific coal type and boiler type. In the derivation of Equation 4-1, the following assumptions are made:

- SO_3 concentrations are proportional to SO_2 concentrations.
- The grade of coal being burned impacts the rate of conversion from SO_2 to SO_3.
- All SO_3 that forms is converted to H_2SO_4.
- The rate of SO_3 formation is independent of the boiler firing rate (unit load).

The estimates of sulfur dioxide emissions (E2) and F1 factors are further described in the following sections.

Sulfur Dioxide (SO_2) Emissions from Combustion (E2)

Estimating the sulfuric acid production from Equation 4-1 requires knowledge of the mass rate of SO_2 generated. This rate is designated as E2 in Equation 4-1. As noted previously, the value of E2 can be estimated from either (a) the EPA CEMS data, or (b) calculated from the coal burn data (EPA, 1995a).

CEMS can directly quantify the annual SO_2 production rate, in tons/year of SO_2. However, it may be necessary to correct for stack geometry in deriving E2. Specifically, if CEMS SO_2 data are used, the factor E2 is defined by the following equation

Equation 4-2a

$$\boldsymbol{E2 = E\left[1 - \frac{\left(C1 * R^2 + C2 * R + C3\right)}{100}\right]}$$

where,

E2 = Corrected SO_2 mass rate, tons per year

E = CEMS-derived SO_2 mass rate, tons per year

C1 = 0.0264 (non-axial flow bias factor)

C2 = 0.183 (non-axial flow bias factor)

C3 = 1.5 (wall effects bias factor) – default value for cylindrical stacks

R = Stack/duct average resultant angle (or swirl angle) from site verification tests, degrees

In equation 4-2a, the factor C3 represents the wall effects bias factor, which is used to specify the non-axial properties of flow within the stack, as measured by EPA Method 1 (EPA, 1991). This value, which will vary with each site, can be determined using EPA Method 2H (EPA, 1999). For most cylindrical stack geometries, a default value of 1.5 can be used; however the R value for each stack can be different and should be determined using the appropriate EPA method. EPA has also proposed a wall effects correction for stacks with rectangular ducts that are equipped with flow monitors (EPA, 2009). This proposal has not been finalized as of December, 2009, but some facilities may be allowed to apply this approach as a conditional test method.

As an alternative to using CEMS data, the following relationship based on coal burn data can be used to estimate the rate of SO_2 emissions:

Equation 4-2b $\mathbf{E2 = K1 \bullet K2 \bullet C1 \bullet S1}$

where,

E2 = SO_2 mass rate, tons/yr

C1 = Dry coal burn, tons/yr. The dry coal can be calculated from wet coal through the following relationship:
Dry coal (tons/yr) = wet coal (tons/yr) • (1-moisture(%)/100%)

S1 = Coal sulfur weighted average, %, dry

K1 = Molecular weight and units conversion constant
= (64.04)/(100 • 32.06) = 0.02
64.04 = molecular weight of SO_2
32.06 = molecular weight of S
conversion of % S to a fraction - multiply by 100

K2 = Sulfur conversion to SO_2, implicit from EPA AP-42 (EPA, 1995b)
= 0.95 for bituminous coals
= 0.875 for subbituminous coals
= 0.55 to 0.85 for lignite, based on the Na content
= 1.0 for oil

When any source uses FGD equipment or another technology to control SO_2 emissions, either the fuel basis <u>must</u> be used for the manufacturing and release calculations, or CEMS data can be used, but only when the CEMS <u>precedes</u> the FGD or SO_2 control equipment. <u>Data from a CEMS located after a flue gas desulfurization system cannot be used.</u>

<u>Fuel Impact Factor (F1)</u>. Figure 4-1 depicts the fraction of H_2SO_4 produced as a function of flue gas SO_2 content for several coal sources and boiler types. The coal ranks and boiler types consist of (a) high sulfur (>2.5%) eastern bituminous coal, fired in a dry bottom boiler (wall-fired or cell-fired), (b) low sulfur eastern bituminous coal, fired in a dry bottom boiler, (c) PRB coal, fired in both a cyclone and dry bottom boilers and (. Data are also shown for one unit that fires 75% lignite with the balance PRB and one unit that fires 100% lignite.

Figure 4-1 shows that a wide range in SO_3 production is observed for all coals and boiler types. This range exceeds the theoretical predictions by Senior (2002), suggesting that the role of ash in either catalyzing SO_3 production or absorbing/neutralizing SO_3 is not fully accounted for. The only consistent results in Figure 4-1 are for SO_3 from PRB-fired units, regardless of boiler type, in that less than 1 ppm was observed.

The previous version of the model (EPRI, 2008) separated eastern bituminous coal data for dry-bottom boilers into two distinct fuel groups, one for low-sulfur (<2.5% coal sulfur) coal and one for high-sulfur (>2.5% coal sulfur) coal. A unique F1 factor was assigned to these two coal types that was the average SO_3 fraction produced for each type. However, that approach led to large fluctuations in estimated sulfuric acid releases for facilities with coal sulfur near the 2.5%

division point. Therefore, the current model replaces the two eastern bituminous coal groups with a linear relationship. The regression line for all eastern bituminous, dry bottom boiler data is shown in Figure 4-1. The equation expressing this relationship is shown in Equation 4-3. This relationship is significant at the 95% confidence level, although the correlation coefficient (R^2) is low (0.13) due to scatter in the data. The current model retains F1 factors based on average fraction of SO_2 converted to SO_3 for all other coal types.

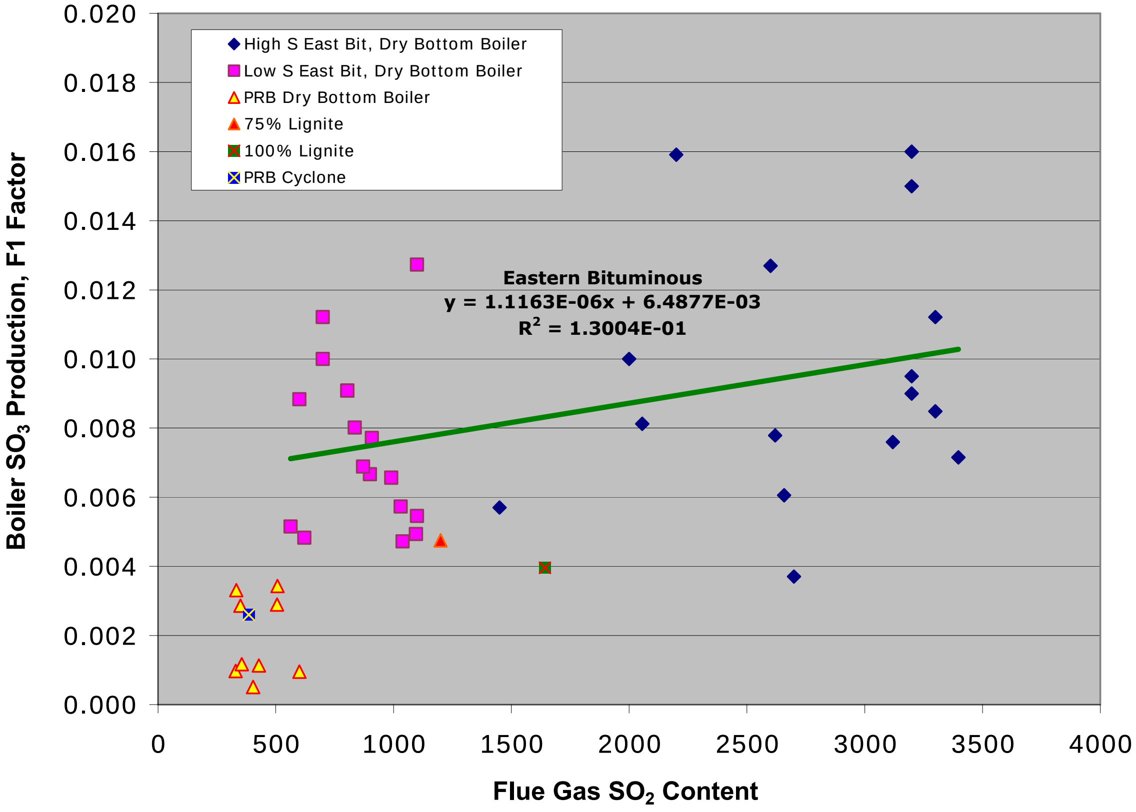

Figure 4-1
Relationship between Boiler SO_3 Production and Flue Gas SO_2 (corrected to 3% O_2)

Equation 4-3 $F1_{ebit} = 1.1163E\text{-}6 \bullet SO2 + 0.0064877$

where,

$F1_{ebit}$ = Fuel Impact Factor for all Eastern Bituminous coals burned in a dry-bottom boiler

SO_2 = Boiler SO_2 concentration (ppm), derived from fuel sulfur content (%)

In order to use this approach, it is necessary to relate coal sulfur (%) to the SO_2 concentration in the boiler. Equation 4-4 is used to calculate that relationship:

Equation 4-4 $$SO_2 = S1 \bullet \frac{K_{F1}}{HV}$$

where,

SO_2 = Boiler SO_2 concentration (ppmvd, 3% O_2, dry) derived from fuel sulfur content (%)

S1 = Coal sulfur weighted average, %, dry

K_{F1} = Conversion factor = 10,003,602

HV = Coal heating value, Btu/lb, dry

The conversion factor K_{F1} considers all relevant constants to yield the result in ppm of SO_2. The derivation of this constant is presented in Text Box A.

Text Box A: Derivation of Conversion Factor, K_{F1}. The U.S. Code of Federal Regulations 40, Part 60, Table 19-1 “F Factors for Various Fuels” states that 1 million Btu of heat input for bituminous or subbituminous coal will produce 10,640 wet standard cubic feet of flue gas, defined at 0% oxygen and on a wet basis at 20ºC and 760 mm Hg. Correcting this volume to 3% O_2 on a dry basis (typical of the SO_2 measurement data used in the Fuel Impact Factors correlation) yields a volume of 11,419 scf. The standard volume of one pound mole of any gas is 359 scf, defined at 0ºC and 760 mm Hg. Converting this to the English units standard of 20C (68°F), one pound mole occupies 385.5 standard cubic feet. The value 0.95 is the AP-42 (EPA, 1995b) K2 factor for sulfur conversion to SO_2 for a bituminous coal.

Equation 4-4 above can then be expanded as follows:

S1%	0.95	385.5 scf S	1 lb mol S	1 MBtu	1 lb fuel	10^6 Btu	10^6 ppm
	100%	1 lb mol S	32.06 lbs S	11,419 scf	HV Btu	1 MBtu	

Grouping terms,

$$SO_2 = S1 \bullet 10{,}003{,}602 / HV$$

Therefore, the value of K_{F1} is equal to 10,003,602 [ppmvd SO_2 (3% O_2, dry) • Btu/lb]/%S.

Table 4-1 summarizes the F1 factors, noting any significant changes from the last version of the model (EPRI, 2008).

Table 4-1
Summary of Fuel Impact Factors (F1) for Steam Generating Units

Fuel	Equipment	F1	Comment
E. Bituminous (all)	Dry Bottom Boiler	Slope: 1.1163E-6 Intercept: 0.0064877	F1 = slope * SO_2 + intercept 32 data points*
Med-High S Eastern Bituminous (>2.5%)	Cyclone	0.016	One data point.
W. Bituminous	Dry Bottom Boiler	0.00111	One data point.
W. Bituminous	Cyclone	0.0022	One data point.
Subbituminous/PRB	All Boilers	0.0019*	Average of 8 units
Lignite	Dry Bottom Boiler	0.0044*	Two data points.
Lignite	Cyclone	0.00112	One data point.
Petroleum coke	Boiler	0.04	One data point.
Natural gas	Boiler	0.01	
#2 Fuel oil	Boiler	0.01	
#6 Fuel oil	Boiler	0.025	
Used oil	Boiler	0.0175	
Natural gas	CT	See Table 6-1	
#2 Fuel oil	CT	See Table 6-1	
Natural gas	CC	0.0555	
#2 Fuel oil	CC	0.0555	
Other Alternative Fuels	Any	0.04	
Other Alternative Fuels, co-fired w/coal, >75% heat throughput	NA		Use Coal F1, in absence of any applicable data.

* Change in factor from EPRI, 2008

Sulfuric Acid Released from Combustion (ER_{Comb})

For units that do not employ SCR or SNCR NOx control or FGC, the sulfuric acid released is the product of the amount manufactured and Technology Impact Factors (F2) for all downstream equipment (the air heater, the particulate control device, the FGD, etc. – described later in Section 4). For these units, the total sulfuric acid emissions can be calculated from Equation 4-5.

Equation 4-5 $$ER_{Comb} = EM_{Comb} \bullet F2 \text{ (all that apply)}$$

Units that do employ SCR or SNCR, and/or flue gas conditioning, must consider these additional sources as described in the following sections.

Text Box B summarizes calculations for units equipped with an FGD process that employs partial flue gas bypass, which must account for the fact that the entire flue gas flow is not subject to sulfuric acid removal by the FGD process. This bypass factor is pertinent only to units that employ flue gas bypass.

Text Box B: Flue Gas Desulfurization Bypass Calculation. Those units equipped with scrubbers where some of the flue gas bypasses the scrubber should take this into account in their combustion release calculations. No credit for sulfuric acid removal should be taken for the fraction of the flue gas that bypasses the scrubber. Therefore, this amount of the flue gas should not be multiplied by the F2 factor for the scrubber. However, the flue gas volume should still be multiplied by the F2 factors for the other control devices.

A modified equation considering partial scrubber bypass is given below and should be used where appropriate.

$$ER_{COMB} = [SB_f + (1 - SB_f) \bullet F2_s] \bullet K \bullet F1 \bullet E2 \bullet F2_x$$

where, SB_f = fraction of scrubber bypass, as a decimal

$F2_s$ = F2 for scrubber

$F2_x$ = All other applicable F2 factors except for scrubber.

Manufacture and Release from SCR and SNCR

This section describes a method to estimate impacts of SCR or SNCR on sulfuric acid emissions. SCR can contribute to or reduce sulfuric acid emissions, while SNCR will only reduce such emissions.

As discussed in Section 3, SCR produces SO_3 (and ultimately sulfuric acid), while SNCR removes or reduces it due to the reaction with residual ammonia. The sulfuric acid manufactured by SCR is the net result of production by the catalyst and removal by the reaction of residual NH_3 from the SCR process.

A key assumption in the calculation strategy is that residual ammonia from either SCR or SNCR captures all available sulfuric acid in the (ammonium) bisulfate form. The bisulfate form is not reportable under the TRI reporting requirement and thus is not part of the manufacture calculation. If any additional ammonia reacts with the bisulfate, it is of no consequence to the sulfuric acid calculation – although this issue will be important when estimating ammonia releases.

The calculations for the manufacture of sulfuric acid by SCR and the release of sulfuric acid by SCR and SNCR are described in the following sections.

Sulfuric Acid Manufacture by SCR (EM_{SCR})

The following relationship estimates the total H_2SO_4 manufactured from an SCR equipped utility boiler or steam generator:

Equation 4-6 $$\mathbf{EM_{SCR} = K \bullet S2 \bullet f_{sops} \bullet E2 \bullet F3_{SCR}}$$

where,

EM_{SCR} = Total H_2SO_4 manufactured from SCR, lbs per year

K = Molecular weight and units conversion constant
= 98.07 / 64.04 • 2000 = 3,063

98.07 = Molecular weight of H_2SO_4

64.04 = Molecular weight of SO_2

Conversion from tons per year to pounds per year – multiply by 2000.

S2 = SCR catalyst SO_2 oxidation rate (specified as a fraction, typically from 0.001- 0.03)

f_{sops} = Operating factor of SCR system, or the fraction of coal burn when the flue gas is directed through the SCR, whether NH_3 reagent is injected to derive NOx reduction or not. This value should reflect the hours the SCR reactor processed flue gas, which will be site-specific but can be approximated by generally 0.8 for year-round peaking operation, 0.98 for year-round base-loaded operation, or 0.43 for seasonal operation

E2 = SO_2 produced, tons per year

$F3_{SCR}$ = Technology Impact Factor, for SCR

The Technology Impact Factor for SCR ($F3_{SCR}$) is required to adjust SO_3 content for the presence of alkaline fly ash, as described in Section 3, unless direct measurements exist for the subject unit documenting SO_3 increase across the SCR reactor.

It is important to select the correct SO_2 oxidation rate for use in Equation 4-6. Typically, the SO_2 oxidation rate from SCR catalysts can range from as low as 0.3% of flue gas SO_2 content, up to 3% for low sulfur, highly alkaline coals (e.g., PRB). There are two means by which SO_2 oxidation is specified and measured for SCR process equipment, and each has significantly different implications for SO_3 produced. One method – based on actual field tests in commercial units – does not require adjustment and can be used as reported to predict sulfuric acid. The other method is based on laboratory tests of catalyst samples in the absence of ash and alkaline materials, and must be adjusted to account for these latter factors. The consequences of each of these methods on estimates of sulfuric acid emissions are described as follows:

Full-Scale Catalyst Performance Tests. Ideally, SO_2 conversion data will be determined with commercial testing of full-scale equipment. These data – measured on commercial plants under actual operating conditions – are the most authentic in reflecting actual SO_3 content, as the impact of ash alkalinity is taken into account. This approach reflects commercial process operation, and the resulting fractional oxidation rate can be used as the S2 value in Equation 4-6 without adjustment by the $F3_{SCR}$ Technology Impact Factor.

Laboratory Bench-Scale Tests. Some owners and process suppliers prefer to specify and conduct guarantee measurements for SO_2 oxidation on laboratory-scale equipment using synthetic flue gases without fly ash. There are good reasons to select this methodology; evidence suggests SO_3 measurements in the environment of the test laboratory are more accurate and reproducible than field tests. However, this method does not expose the catalyst being tested to ash, so there is no alkaline component to mitigate or absorb any SO_3 generated. Accordingly, SO_2 oxidation reported by this method exceeds that measured in commercial practice, particularly for PRB coals. SO_2 oxidation data from bench-scale tests can be used, but must be adjusted for the role of ash alkalinity. This adjustment is provided by the Technology Impact factor $F3_{SCR}$.

An $F3_{SCR}$ factor for PRB coals is shown in Table 4-2. This factor is derived from measurements at two PRB-fired units. SO_3 emitted from these units was lower than specified in the catalyst guarantee, which was based on laboratory test data. At present, there are no data to support $F3_{SCR}$ factors for other coals, so a factor of 1 (full penetration) is recommended.

Table 4-2
$F3_{SCR}$ Technology Impact Factors for SCR

Coal Type	$F3_{SCR}$
PRB	0.17
Other Coals	1 (no data available)

SNCR will not result in the manufacture of sulfuric acid, thus EM_{SNCR} is by definition zero.

Sulfuric Acid Released from SCR and SNCR

The sulfuric acid released from SCR or SNCR is determined by subtracting from the sulfuric acid manufactured the amount removed by the residual ammonia, or ammonia slip. For SCR, the sulfuric acid released (ER_{SCR}) is estimated with the following relationship:

Equation 4-7 $$ER_{SCR} = [EM_{SCR} - (K_s \bullet B \bullet f_{sreagent} \bullet S_{NH3})] \bullet F2_x$$

where,

ER_{SCR} = Total H_2SO_4 released from SCR, lbs per year

EM_{SCR} = Total H_2SO_4 manufactured from SCR, lbs per year

K_s = Conversion factor = 3799 (See Text Box C)

B = Coal burn in TBtu/yr

$f_{sreagent}$ = fraction of SCR operation with reagent injection, when residual NH_3 is produced that will remove SO_3. The value of $f_{sreagent}$ will be similar to, but slightly less than, the value of f_{sops}, defined for Equation 4-6.

S_{NH3} = NH_3 slip from SCR/SNCR, ppmv at 6% O_2, wet:

- SCR averages 0.75 ppmv over catalyst guarantee period
- SNCR averages 5 ppmv
- Note: actual NH_3 slip data should be used if available

$F2_x$ = Technology Impact Factors, all that apply

The conversion factor K_s, equal to 3799, considers all relevant constants to yield the result in pounds per year of sulfuric acid. The derivation of this constant, for the case where residual NH_3 is reported in terms of 6% oxygen and "wet" flue gas at 8.1% H_2O, is presented in Text Box C.

Text Box C: Derivation of Conversion Factor, K_s. The U.S. Code of Federal Regulations 40, Part 60, Table 19-1 "F Factors for Various Fuels" lists that 1 million Btu of heat input for bituminous or subbituminous coal will produce 10,640 wet standard cubic feet of flue gas, defined at 0% oxygen and on a wet basis at 20C and 760 mm Hg. Correcting this volume to 6% O_2 (typical at ESP conditions) yields a volume of 14,925 scf. The standard volume of one pound mole of any gas is 359 scf, defined at 0C and 760 mm Hg. Converting this to the English units standard of 20C (68°F), one pound mole occupies 385 standard cubic feet. Using these in the equation above,

$(K_s \bullet B \bullet f_s \bullet S_{NH3})$ = lbs H_2SO_4 per yr =

B TBtu	S_{NH3} scf NH_3	1 lb mol NH_3	1 lb mol H_2SO_4	98 lbs H_2SO_4	14925 scf fg	10^6 MBtu
year	10^6 scf flue gas	385 scf NH_3	1 lb mol NH_3	1 lb mol H_2SO_4	1 MBtu	TBtu

Grouping terms,

$= B \bullet f_s \bullet S_{NH3} \bullet 3799$

Therefore, the value of K_s is equal to 3799 lbs H_2SO_4/(TBtu • ppmv NH_3 @ 6% O_2 and wet).

Equation 4-7 specifies the concentration of NH_3 in flue gas (S_{NH3}) in terms of ppmv at 6% O_2, wet flue gas basis. If the concentration of NH_3 is reported at different conditions, the value of the constant K_s will change. The following formula is used to adjust the value of the constant K_s:

Equation 4-8a $Ks\ (O_2, H_2O\ ) = 3799\ (6\%\ O_2, 8.1\%\ H_2O) \bullet [(100-8.1)/(100\text{-new } H_2O)] \bullet [(20.9 - 6.0)/(20.9 - \text{new } O_2)]$

For example, if the ammonia concentration is quantified at a value (in ppm) that is defined at 0% oxygen and a dry basis, the value of K_s that should be used is:

Equation 4-8b $Ks\ (O_2, H_2O) = 3799\ (6\%\ O_2, 8.1\%\ H_2O) \bullet [(100-8.1)/(100-0)] \bullet [(20.9 - 6.0)/(20.9 - 0)]$

$Ks = 2489$

Equation 4-8a can be used to calculate the value of K_S at any condition used to define the concentration of residual NH_3.

The operating factor of the SCR describes the portion of the coal burn that reflects the period of SCR operation, based on whether the unit operates seasonally (0.43), annually in a base-load duty (0.98), or annually in peaking duty (0.80).

The coal burn rate in TBtu/yr can be obtained from coal use records, such as those reported to EIA in Form 767, or can be calculated from the annual coal burn (tons/yr) and the heating value of the coal, as described in the equation below:

Equation 4-9 $\mathbf{B = C1 \bullet HV \bullet K_B}$

where,

B = Coal burn in TBtu/yr

C1 = Dry coal burn, tons/yr. The dry coal can be calculated from wet coal through the following relationship:
Dry coal (tons/yr) = wet coal (tons/yr) • (1-moisture(%)/100%)

HV = Coal heating value, Btu/lb, dry

K_B = Conversion factor = 2E-9. The factor is calculated from the conversion of tons per year to pounds per year and Btu to TBtu ($2000/10^{12}$ = 2E-9)

For SNCR, as there is no sulfuric acid manufacture term; the sulfuric acid release due to SNCR (ER_{SNCR}) is a negative amount which, when included in the calculations, will result in an overall reduction of sulfuric acid emissions.

Accordingly, total sulfuric acid release (TSAR) for a generating unit equipped with SCR is estimated by the following equation:

Equation 4-10 $\mathbf{TSAR = ER_{Comb} + ER_{SCR}}$

Total sulfuric acid release (TSAR) for a generating unit equipped with SNCR is estimated by the following equation:

Equation 4-11 $\mathbf{TSAR = ER_{Comb} + ER_{SNCR}}$

For units equipped with flue gas desulfurization bypass, a series of calculations analogous to those described in the previous section for combustion-derived sulfuric acid are required. The calculations for SCR or SNCR are described in Text Box D.

<u>*Text Box D: Special Provision for Flue Gas Desulfurization Bypass*</u>. Those units equipped with scrubbers where some of the flue gas bypasses the scrubber should take this into account in their SCR/SNCR release calculations also, as in the combustion release calculations. No credit for sulfuric acid removal should be taken for the fraction of the flue gas that bypasses the scrubber. Therefore, this amount of the flue gas should not be multiplied by the F2 factor for the scrubber. However, it should still be multiplied by the F2 factors for the other control devices.

A modified equation considering partial scrubber bypass is given below and should be used where appropriate.

$$ER_{SCR} = [SB_f + (1 - SB_f) \bullet F2_s] \bullet [EM_{SCR} - (K_s \bullet B \bullet f_s \bullet S_{NH3})] \bullet F2_x$$

where,

SB_f = fraction of scrubber bypass, as a decimal

$F2_s$ = F2 factor for scrubber

$F2_x$ = All other applicable F2 factors except for scrubber.

Manufacture and Release from Flue Gas Conditioning (FGC)

Sulfuric Acid Manufactured from FGC

In order to moderate ash resistivity, most SO_3–based FGC systems attempt to maintain a fixed concentration of SO_3 in the flue gas, typically between 5 and 7 ppm by volume (ppmv). Calculations to estimate the sulfuric acid manufactured during FGC use the setpoint of the FGC system as the key input. The FGC system is assumed to operate during most of the plant's duty, except for perhaps startup and low load operation. The sulfuric acid manufactured by SO_3-based FGC equipment (EM_{FGC}) is calculated as follows:

Equation 4-12 $$\mathbf{EM_{FGC} = K_e \bullet B \bullet f_e \bullet I_s}$$

where,

EM_{FGC} = Total H_2SO_4 manufactured from FGC, lbs per year

K_e = Conversion factor = 3799, which is equivalent to Ks, as described in Text Box C.

B = Coal burn in TBtu/yr

F_e = Operating factor of FGC system, or the fraction of coal burn when the FGC system operates. This value is site-specific, must be determined for each unit, but generally will be about 0.8.

I_s = SO_3 injection rate in ppmv at 6% O_2, wet; generally,

= 7 ppmv if before the APH

= 5 ppmv if after the APH

If the SO_3 injection rate (I_S) is known at conditions other than 6%O_2 and wet, Equation 4-8a can be used to calculate a new value K_e at the new conditions.

FGC equipment that employs both SO_3 and NH_3 must be reported to manufacture sulfuric acid at the rate of SO_3 injection, regardless of whether ammonia is used or not. FGC equipment that employs NH_3 alone does not manufacture sulfuric acid, and any ammonia will reduce the release of sulfuric acid by reacting with SO_3 or the resultant H_2SO_4. The reduction in flue gas sulfuric acid by reaction with ammonia determines the sulfuric acid released by FGC, as discussed in the next section.

Sulfuric Acid Released from FGC (ER_{FGC})

The subsequent release of sulfuric acid associated with flue gas conditioning can be estimated from the sulfuric acid quantity manufactured, adjusted by the amount that reacts with ammonia in any particulate control device installed downstream of the FGC.

Equation 4-13 $$\mathbf{ER_{FGC} = [EM_{FGC} - (K_e \bullet B \bullet f_e \bullet I_{NH3})] \bullet F3_{FGC} \bullet F2}$$

where,

ER_{FGC} = Total H_2SO_4 released from FGC, lbs per year

EM_{FGC} = Total H_2SO_4 manufactured from FGC, lbs per year

K_e = Conversion factor = 3799, which is equivalent to Ks, as described in Text Box C

B = Coal burn in TBtu/yr

F_e = Operating factor of FGC system, or the fraction of fuel burn when the FGC system operates. This value will be the same as F_e described previously and in many cases can be approximated by 0.8.

I_{NH3} = NH_3 injection for dual flue gas conditioning, ppmv at 6% O_2, wet; generally 3 ppmv NH_3 if operating, or zero (0) if no ammonia is used.

$F3_{FGC}$ = Technology Impact Factors for FGC, see Table 4-3

F2 = Technology Impact Factors for equipment after the ESP only, if no control equipment is installed after the ESP; F2 = 1.

Table 4-3
$F3_{FGC}$ – Technology Impact Factors for FGC with Cold-Side ESP

Location	**Coals**	**$F3_{FGC}$**
Upstream of APH	Bituminous	0.25
Upstream of APH	W. bituminous, subbituminous, & lignite	0.05
Downstream of APH	Bituminous	0.10
Downstream of APH	W. bituminous, subbituminous, & lignite	0.02
For other fuels, use F3 = 0.5 for startup fuel and F3 = coal factor for fuels co-fired as a minor fraction (<25%) with coal.		

This approach leads to a possible contradiction in the behavior of SO_3/H_2SO_4 depending on the place in which the SO_3/H_2SO_4 enters the system. Depending on the source of the SO_3, and for FGC, where it is injected, the predicted removal within the air heater and ESP can differ. No mechanistic reason has been identified for these differences in removal – they emerge from the supporting data.

For SO_3 manufactured by combustion, SCR, or introduced as FGC ahead of the air preheater, the method predicts sulfuric acid removal of 75% ($F3_{FGC} = 0.25$) for eastern bituminous coals across an air preheater/cold-side ESP combination. However, as denoted in Table 4-3, a higher fraction of SO_3 or H_2SO_4 (90%, $F3_{FGC} = 0.10$) is predicted to be removed for FGC if injected downstream of the air preheater. The difference in results is likely attributable to the limited number of data points and uncertainty in the measurements. It is recommended that the methodology be executed as described, and future versions will attempt to resolve this difference.

For western or low-rank fuels, SO_3 injected ahead of the air heater as FGC is assumed to be 95% removed ($F3_{FGC} = 0.05$) through the air heater and ESP. SO_3 is assumed to be 98% removed ($F3_{FGC} = 0.02$) when injected downstream of the air heater. As these western bituminous, subbituminous, and lignite coals feature significant alkaline content of ash, any SO_3 injected for FGC will likely be captured by both physical deposition and chemical reaction. Accordingly, it is reasonable that SO_3/H_2SO_4 removal assumed for these coals be higher than for eastern bituminous coals. Further, as the injection of SO_3 on the cold-side of the air preheater is typically below the acid dewpoint, it can be expected that any injected SO_3 will condense on fly ash more readily compared to the slower cooling of the flue gas through the air preheater.

For units equipped with flue gas desulfurization bypass, a series of calculations analogous to those described in the previous sections for combustion- and SCR-derived sulfuric acid are required. These calculations for FGC are described in Text Box E.

Text Box E: Special Provision for Flue Gas Desulfurization Bypass. Those units equipped with scrubbers where some of the flue gas bypasses the scrubber should take this into account in their FGC release calculations also, as in the combustion and SCR/SNCR release calculations. No credit for sulfuric acid removal should be taken for the fraction of the flue gas that bypasses the scrubber. Therefore, this amount of the flue gas should not be multiplied by the F2 factor for the scrubber. However, it should still be multiplied by the F2 factors for the other control devices.

A modified equation considering partial scrubber bypass is given below and should be used where appropriate.

$$ER_{FGC} = [SB_f + (1 - SB_f) \bullet F2_s] \bullet [EM_{FGC} - (K_e \bullet B \bullet f_e \bullet I_{NH3})] \bullet F3_{FGC} \bullet F2_x$$

where,

SB_f = fraction of scrubber bypass, as a decimal

$F2_s$ = F2 factor for scrubber

$F2_x$ = All other applicable F2 factors except for scrubber.

Total Manufacture and Release for Source

For any given source, the total manufacture and release of sulfuric acid is the sum of the individual manufacture or release estimates. Therefore, if a site burns coal and uses both SCR and FGC, the amount of sulfuric acid manufactured – by combustion, SCR, and/or FGC – is added together to determine the total amount. The amount of sulfuric acid released is also calculated – again for combustion, SCR, and FGC – and summed to define the total.

Both SCR and/or ammonia-based FGC may have a negative effect on sulfuric acid release, as the ammonia slip can combine with some or all of the sulfuric acid generated from combustion to form a non-reportable ammonia salt (ABS or AS). Under these conditions, ammonia-based FGC can serve to only reduce the release of sulfuric acid. Since the release of sulfuric acid from combustion, SCR, and FGC are all additive, any negative values calculated as a result of these circumstances will need to be accounted for in the total release equation.

Accordingly, total sulfuric acid manufacture (TSAM) and release (TSAR) is estimated for a generating unit equipped with SCR and flue gas conditioning by the following equations:

Equation 4-14a: Manufacture

$$\mathbf{TSAM = EM_{Comb} + EM_{SCR/SNCR} + EM_{FGC}}$$

Equation 4-14b: Release

$$\mathbf{TSAR = ER_{Comb} + ER_{SCR/SNCR} + ER_{FGC}}$$

Examples 1 through 4 in Appendix A detail the use of these calculations.

Total Release Calculation for Sources Employing Alkali Injection

As described in Section 3, sources that employ alkali injection to mitigate stack opacity or a visible plume will have access to field measurements describing SO_3 concentration in flue gas, most likely at the stack. The concentration of SO_3 measured at the stack can be converted to a mass emission rate using Equation 4-15

Equation 4-15 $\mathbf{ER_{ALKINJ} = K_{alkali} \bullet B \bullet S_{SO3} \bullet F2_x \bullet F_{alkali}}$

where,

ER_{ALKINJ} = Total H_2SO_4 released from unit equipped with alkali injection, lbs per year

K_{alkali} = Constant, equal to 3,799, which is equivalent to Ks, as described in Text Box C.

B = Coal burn in TBtu/yr

S_{SO3} = SO_3 content, as measured in the stack or particulate collector exit, ppmv at 6% O_2, wet

F_{alkali} = fraction of time unit is operated with alkali addition to remove SO_3

$F2_x$ = Technology Impact Factors, to be applied only if SO_3 measurements are conducted at a location preceding the stack. The value of $F2_x$ is 1 if measurements are conducted at the stack, and there are no control components downstream of the measurement location. If the control device is an SO_2 scrubber, F2x is denoted as F2s, but is handled the same way.

If the SO_3 content (S_{SO3}) is known at conditions other than 6%O_2 and wet, Equation 4-8a can be used to calculate a new value K_{alkali} at the new conditions.

The Technology Impact Factors selected should represent the control equipment between the point of SO_3 measurement and the stack. For example, if a unit is equipped with only an ESP, and the SO_3 measurement is conducted at the ESP inlet, then the F2 factor for an ESP (Table 4-4, below) should be selected.

If alkali injection is not utilized for the entire operating year (F_{alkali} does not equal 1), then Equation 4-15 must be added to the fraction of the total sulfuric acid release (TSAR) calculated from combustion, SCR/SNCR and/or FGC for the remainder of the operating time. Furthermore, in the calculation of TSAR for partial-year alkali injection, if SO_3 measurements also exist for operation without alkali injection, these data should be used with Equation 4-15 (without the F_{alkali} term) instead of the standard estimation equations to determine the term: ER_{Comb} + $ER_{SCR/SNCR}$ + ER_{FGC}, as shown below:

Equation 4-16 $$ER_{NOINJ} = K_{alkali} \bullet B \bullet S_{SO3} \bullet F2_x \bullet (1-F_{alkali})$$

where,

ER_{NOINJ} = Total H_2SO_4 released from unit without alkali injection, lbs per year

K_{alkali} = Constant, equal to 3,799, which is equivalent to Ks, as described in Text Box C.

B = Coal burn in TBtu/yr

S_{SO3} = SO_3 content without alkali injection, as measured in the stack or particulate collector exit, ppmv at 6% O_2, wet

F_{alkali} = fraction of time unit is operated with alkali addition to remove SO_3

$F2_x$ = Technology Impact Factors, to be applied only if SO_3 measurements are conducted at a location preceding the stack. The value of $F2_x$ is 1 if measurements are conducted at the stack, and there are no control components downstream of the measurement location. If the control device is an SO_2 scrubber, F2x is denoted as F2s, but is handled the same way.

Accordingly, total sulfuric acid release (TSAR) for a unit employing partial-year alkali injection is estimated by one of the following equations:

Equation 4-17a $$TSAR = ER_{ALKINJ} + (ER_{Comb} + ER_{SCR/SNCR} + ER_{FGC}) \bullet (1-F_{alkali})$$

Equation 4-18b $\mathbf{TSAR = ER_{ALKINJ} + ER_{NOINJ}}$

Technology Impact Factors (F2)

The sulfuric acid estimating methodology employs empirically-derived Technology Impact Factors (F2). These F2 factors describe sulfate removal observed over the air heater, the ESP or other particulate control device, and FGD process equipment. Background information on these processes and the derivation of these F2 factors are addressed in this section.

Air Heater

The removal of SO_3 and/or H_2SO_4 within the air heater is due to the condensation of sulfuric acid and its removal as discrete individual particles (along with the fly ash) on the surface of this heat exchanger. The conventional Ljungstrom-type air heater has been documented to provide a removal sink for sulfuric acid (Saranuc, 1999). In fact, the largest supplier of Ljungstrom air heaters has evaluated the feasibility of employing the air heater process environment in conjunction with limestone injection as a proactive sulfuric acid control strategy (Hamel, 2003, and Bowes, 2006).

Air heater surfaces follow a pattern of alternately heating and cooling as the heat exchange elements move from the relatively hot flue gas to the cooler combustion air. As reported during field tests of commercial equipment (Saranuc, 1999), this temperature profile introduces a strong gradient in sulfuric acid concentration across the exit plane of the air heater. The cyclic thermal conditions as described by Hamel (2003) reveal that a significant portion of the air heater basket surface metal is exposed to flue gas temperature below the sulfuric acid dewpoint. This phenomenon may promote sulfuric acid deposition on the heat exchanger metal surface, compared to a tube-type heat exchanger in which the metal temperature is always above the sulfuric acid dewpoint.

Figure 4-2 presents data obtained from a survey of power plant operators and general literature sources describing SO_3/H_2SO_4 removal (and the corresponding F2 factors) across commercial, Ljungstrom-type air heaters. These data are presented as a function of SO_2 content of the flue gas for the host unit. Most data shown are for low sulfur eastern bituminous coal, for which air heater H_2SO_4 removal varies significantly between 0% and 69%, averaging 50% as indicated by the horizontal line. Two high sulfur (>2.5%) eastern cases are shown, along with limited data for PRB coal.

The data point showing 0% removal at approximately 600 ppm SO_2 is believed suspect, as an identical companion unit firing the same coal exhibited sulfuric acid capture of 38%. This measurement was not included in the F2 calculation.

Figure 4-2 presents two points reported by Hamel (2003) based on a low sulfur eastern bituminous-fired unit where SO_3 was "spiked" into the flue gas to elevate the concentration entering the air heater to 80 and 122 ppm. These two points are plotted separately on Figure 4-2 versus an estimated flue gas SO_2 content that could generate such values (using the average SO_2 oxidation rate for high sulfur, eastern bituminous coal in Figure 4-1). It should be noted these values measured for the "spiked" flue gas significantly exceed those measured for the two high sulfur eastern coal cases.

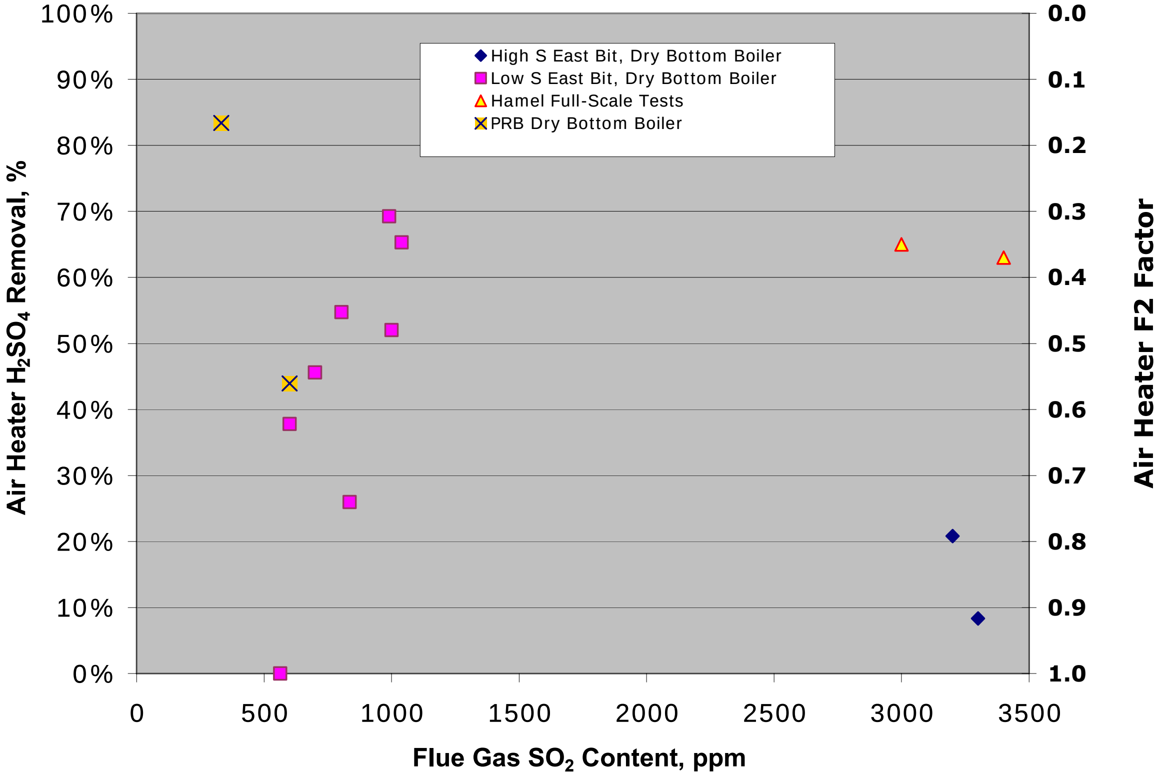

Figure 4-2
Removal of Sulfuric Acid by Ljungstrom-Type Air Heaters

The F2 factor for the air heater, calculated as [1 – Percent Removal], is estimated excluding the "spiked" SO_3 and suspect 0% removal measurement. The F2 factors for the air heater for low sulfur eastern bituminous, medium-high sulfur eastern bituminous, and PRB coals are shown in Table 4-3. Data are not currently available for other coal types. For those coals, the model user could consider adopting the F2 factor for PRB if the ash is strongly alkaline and the low sulfur, eastern bituminous value if the ash is acidic.

Table 4-3
Summary of F2 Factors for Air Heater Removal of Sulfuric Acid

Boiler Type	Fuel	F2	Standard Deviation	Comment
All Boilers	Low S Eastern Bit	0.50*	0.15	Average of measurements at 7 units.
All Boilers	Med-High S Eastern Bit (S >2.5%)	0.85	n/a	Based on two data points.
All Boilers	PRB	0.36*	n/a	Based on two data points.

* Change in factor from EPRI, 2008.

The standard deviation of the reported measurements for low sulfur eastern bituminous coal is about one third of the average measurement. There are not enough data to calculate a standard deviation for the F2 factors for the other fuels.

Particulate and SO_3 Control Processes

This section discusses the available data on removal of SO_3 by ESPs, FGDs, and alkali injection.

ESPs and Baghouses

An ESP provides extended residence time at relatively low temperatures, allowing contact between sulfuric acid and fly ash particles, as well as having collecting plates that can retain sulfuric acid particles. These features contribute to the removal of sulfuric acid. The ESP is the flue gas contacting device with perhaps the longest residence time; for large units, usually 10 seconds and in some cases up to 15 seconds. Given the low flue gas velocities of 2 to 4 actual feet per second (0.6 – 1.2 meters per second), and the opportunity for heat loss at or near the walls, sulfuric acid condensation can be significant.

Figure 4-3 plots sulfuric acid removal by the ESP and the corresponding F2 factors as a function of the SO_2 content of the flue gas for the host unit, from a survey of plant operators. Most data shown are for a cold–side ESP and low sulfur eastern bituminous coal; three data points are shown for high sulfur coal (>2.5%). Also shown is a single data point for a hot-side ESP and four data points for low sulfur eastern bituminous coal. Similar to the case for the air heater, the 0% sulfuric acid removal at approximately 800 ppm SO_2 is suspect, as a companion unit at the same site firing the identical coal had 50% sulfuric acid removal. Accordingly, this “zero” removal datum, although shown in Figure 4-3, is not used in the analysis.

The F2 factor for the cold-side ESP, calculated as [1- Percent Removal], is estimated using all data except the 0% removal point. The F2 factors for ESP capture for low sulfur eastern bituminous, medium-high sulfur eastern bituminous, and PRB coals are listed in Table 4-4. The F2 factor for the low sulfur eastern bituminous coal has been updated from a value of 0.49 in the 2008 version of the model to 0.63 due to the reevaluation of measurement data from one of the sources. Data are not currently available for other coal types. Facilities using coals not supported by the model should select a F2 factor for a coal with similar alkalinity in the ash: western subbituminous coals (e.g., non-PRB) could consider adopting the F2 factor for PRB if the ash is strongly alkaline; western coals with acidic ash (e.g., bituminous) may consider adopting the low sulfur, eastern bituminous value.

Data describing the reduced H_2SO_4 penetration for one hot-side ESP (ESPh) is based on only a single test series It should be noted that although this F2 factor is used for all coals, the measurement is from a power plant burning a low-sulfur, eastern bituminous coal. Comparison of F2 factors for a cold-side ESP burning low and high sulfur eastern bituminous coals show a significant difference between the two coal types. As a result, total H_2SO_4 releases for hot-side ESP configurations may have a low bias; however there is insufficient data to recommend alternate values.

Data for baghouses show high H_2SO_4 removal based on very limited data from plants burning subbituminous coal. The average of two data points was 90% removal.

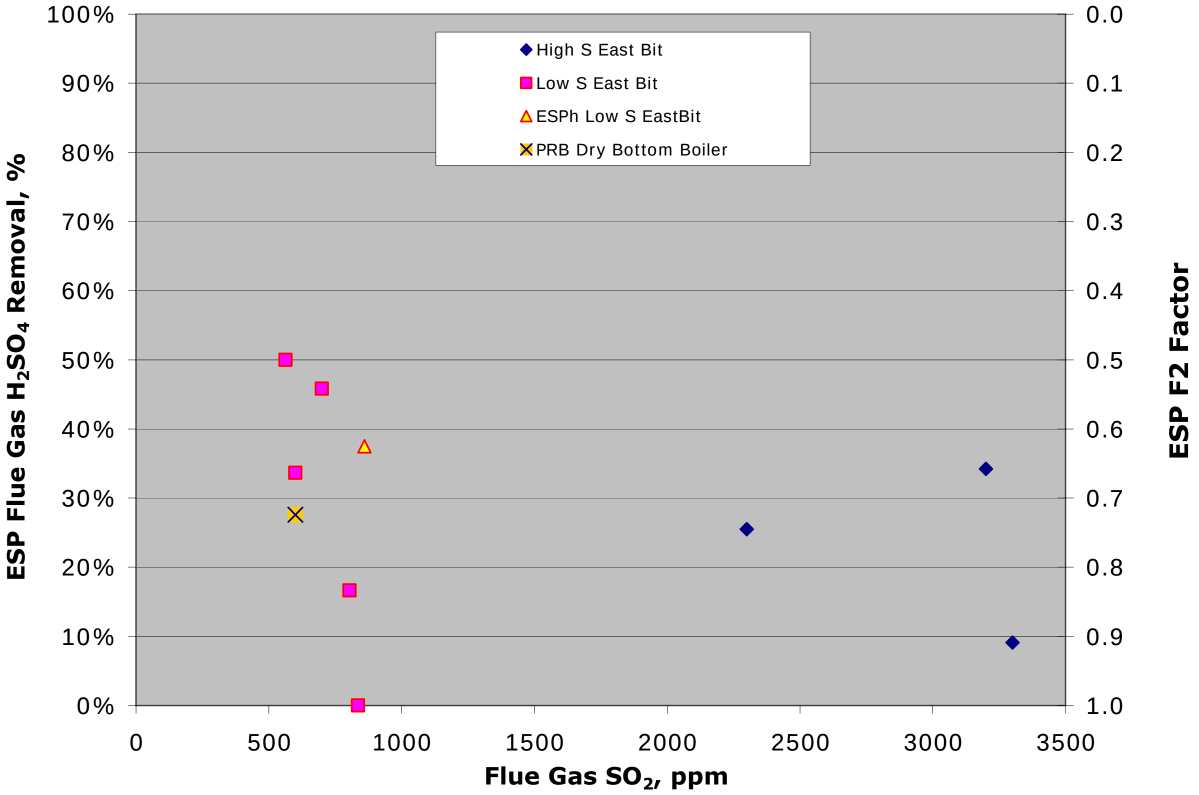

Figure 4-3
Removal of Sulfuric Acid by Cold-Side ESPs and One Hot-Side ESP

Table 4-4
Summary of F2 Factors for Particulate Control Devices (ESP, Baghouse)

Equipment Type	Coal Type	F2 Factor	Standard Deviation	Comment or Observation
Cold-side ESP	Low S Eastern Bit	0.63*	0.15	Average of measurements at 4 units.
Cold-side ESP	High S Eastern Bit (>2.5%)	0.77	0.13	Average of measurements at 3 units.
Cold-side ESP	Subbituminous (PRB)	0.72*	n/a	Based on one measurement at one unit.
Hot-side ESP	All	0.63	n/a	Based on one measurement at one unit.
Baghouse	Subbituminous coal	0.10	n/a	Two data points.

* Change in factor from EPRI, 2008.

The standard deviation of the reported measurements for low sulfur eastern bituminous coal is about one fourth of the average measurement, while the standard deviation of the measurements for the high sulfur eastern bituminous coal is about one sixth of the average. Inadequate data prevent calculating a standard deviation for F2 factors for the other fuels.

FGD

FGD process equipment rapidly cools or quenches flue gas, condensing a significant portion of the sulfuric acid into submicron droplets that can escape the process environment, confounding capture. Buckley (2002) notes that for condensation to occur, sulfuric acid generally must be supersaturated. However, fly ash particles can provide a nucleus for condensation of sulfuric acid, even at conditions that are not thermodynamically supersaturated. Buckley also projects sulfuric acid condensation on surfaces where equipment walls are lower in temperature than the flue gas (common in commercial equipment). However, the thin laminar boundary layer at the wall limits mass transfer, and for FGD equipment this mechanism provides no appreciable removal. Ironically, it is the high saturation conditions in this laminar layer near surfaces that are key to producing fine sulfuric acid mist.

Srivastava (2004) suggests that the condensed submicron droplets, once formed, are sufficiently small so that they follow the flow streamlines and avoid contact with the remaining wetted walls, liquid sheets, and droplets in the flow path. Although some degree of sulfuric acid removal is observed in FGD equipment, the amount is highly variable and depends on the design of the system. Buckley (2002) estimates FGD equipment removes 40-70% of the sulfuric acid, and Srivastava an average of 50%.

Figure 4-4 summarizes data reported in the public domain and from power company sources describing FGD removal (and corresponding F2 factors) of sulfuric acid. The percent of sulfuric acid removal is depicted as a function of FGD inlet SO_2 concentration. Removals range from 22% to 78%, with an average of about 50%. The shaded portion of Figure 4-4 represents the upper and lower bounds of the data reported by Buckley (2002), while the solid horizontal line reflects the 50% average reported by Srivastava (2004).

Table 4-5 summarizes the F2 factors for FGD process equipment, including results for wet spray towers burning bituminous coal. Two results are available for a wet scrubber at a unit burning a blend of PRB/lignite. Harrison (2005) calculated an average removal of 60% for these units. Given the limited data, this value is assumed to apply to 100% firing of PRB or lignite. Data for a wet venturi-type combined particulate/FGD process is also available, but only for a bituminous coal. Similar to the case for a wet spray tower, the lack of data merits assuming sulfuric acid removal for all coals is described by that measured for bituminous coal.

F2 factors for the use of magnesium-based additives in oil-fired boilers are also included in Table 4-5. These additives are used to control furnace slagging caused by the vanadium in the oil or to control sulfuric acid emissions or both. The fuel oil vanadium can also catalyze SO_2 to SO_3 oxidation, but the additive, when added to the oil, tends to effectively bind up the vanadium, partially reducing its catalytic effect. Addition of magnesium-based additives in the fuel oil tend to be less effective in controlling the emissions of sulfuric acid than the same additive sprayed into the furnace downstream of the flame zone.

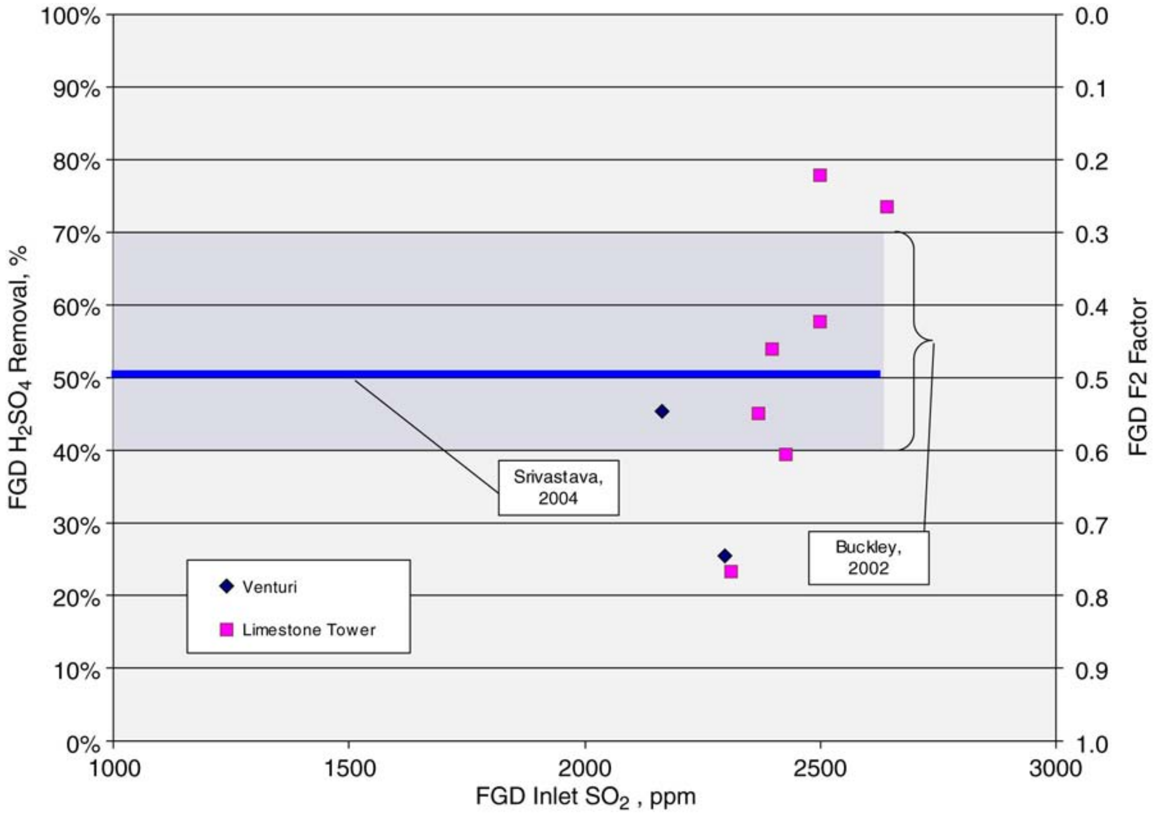

Figure 4-4
Removal of Sulfuric Acid by Flue Gas Desulfurization Equipment: Various FGD Designs, Coals

Table 4-5
Summary of F2 Factors for Wet and Dry FGD Equipment and Additives

FGD Type	Coal Type	F2 Factor	Standard Deviation	Comment or Observation
Wet: Spray Tower	E. Bituminous	0.47	0.17	Seven data points.
Wet: Spray Tower	PRB or Lignite	0.40	n/a	Two data points.
Wet: Venturi Tower	All coals	0.65	n/a	Based on bituminous coal only; limited data from 2 units merit assigning same factor for other coals.
Dry FGD and baghouse	All coals	0.01	n/a	Two data points.
Mg-Ox mixed w/fuel oil	All fuel	0.50	n/a	One data point.
Mg-Ox into furnace	All fuel	0.50	n/a	One data point.

5

ESTIMATING GUIDELINE: MULTIPLE FUEL OR BLENDED FUEL BOILERS

Estimating sulfuric acid production of steam boilers firing multiple or blended fuels – such as natural gas, fuel oil, and perhaps coal – uses the same approach as for single fuels. This will consist of determining the contribution of each source (combustion, SCR or SNCR NOx control, and FGC) for each different fuel, and adjusting for loss or removal. It is assumed for multiple fuel boilers that the contribution of each fuel can be separated and treated individually. The same approach is to be used for boilers that fire a blended coal. This assumption is particularly important when considering blends of PRB with low or high sulfur eastern bituminous coal, as this approach accounts for the role of alkalinity in PRB ash in mitigating SO_3.

This approach of treating blends of coal as separate fuels in proportion to the mass burn rate is believed to be conservative with regard to SO_3 emissions when considering PRB coal, in that it will likely project H_2SO_4 emissions higher than actual. The ability of PRB coal to neutralize SO_3 by an amount that is greater than a direct proportion of the coal blend is due to the extremely high content of alkaline material, particularly CaO. However, data to quantify this impact with any reasonable degree of confidence are not available at present. Accordingly, the conservative approach is to presume an impact in direct proportion to the coal blend until a database can be developed.

The sequence of calculations is performed for the first component of the blend, including calculations for SCR and FGC, if applicable. The sequence is repeated for each component. When complete, the total manufacture of sulfuric acid is calculated by adding all of the manufacture totals for all fuels from all processes. Likewise, the release is summed over all processes and fuels.

As an example, if a unit with an SCR and FGC burns mostly coal, but uses natural gas in a NOx reburn process and also disposes of used oil by combustion in the furnace, then the following sequence of calculations would be required:

1. Coal fuel
   a. Combustion manufacture
   b. Combustion release
   c. SCR manufacture
   d. SCR release
   e. FGC manufacture
   f. FGC release
2. Natural gas
   a. Combustion manufacture
   b. Combustion release
   c. SCR manufacture
   d. SCR release
   e. FGC manufacture

    f. FGC release
3. Used oil
    a. Combustion manufacture
    b. Combustion release
    c. SCR manufacture
    d. SCR release
    e. FGC manufacture
    f. FGC release
4. Sum manufacture and releases
    a. Manufacture

       = 1a + 1c + 1e + 2a + 2c + 2e + 3a + 3c + 3e

    b. Release

       = 1b + 1d + 1f + 2b + 2d + 2f + 3b + 3d + 3f

All of the manufactured results would be summed together and the releases summed also to give the final result. Example 5 in Appendix A details this calculation procedure.

6

ESTIMATING GUIDELINE: COMBUSTION TURBINES

Natural gas-fired sources typically have negligible content of sulfur in the fuel, thus sulfuric acid production is negligible. Facilities that burn only natural gas are not required to participate in the TRI reporting program. However, sources that are co-located with coal units will need to be included in the estimates for total sulfuric acid release for the site. The calculation described in this section can also be used to estimate sulfuric acid emissions for Prevention of Significant Deterioration (PSD) review of new natural gas-fired generation sites.

The calculations for gas-fired units are structured very much the same as for coal- and oil-fired sources. For simple cycle combustion turbines, the only source of sulfuric acid is the sulfur in the fuel. The EPA AP-42 emissions factor suggests a value of 2000 grains of sulfur per million cubic feet of natural gas as a default sulfur content value. This value is equivalent to approximately 3.5 ppm of sulfur in the raw natural gas.

A methodology to estimate manufacture and release of sulfuric acid for simple cycle and combined cycle units is provided below.

Simple Cycle Units

Given the current configuration of simple cycle units, any sulfuric acid ***manufactured*** is ***released***; thus, the estimates of sulfuric acid are the same. This is because there is no equipment located following the simple cycle arrangement that removes sulfuric acid. Even though simple cycle units can be equipped with SCR, and the use of SCR with sulfur-containing fuels will manufacture SO_3, the exit gas temperature is too high to allow condensation of SO_3 or reaction with ammonia slip. Selective non-catalytic reduction (SNCR) is not applied to simple cycle or combined cycle combustion turbines; therefore, no estimation procedure is provided for that configuration.

Accordingly, the equations for formation of sulfuric acid from natural gas (NG) combustion are:

Equation 6-1 $\mathbf{EM_{SC} = K \bullet F1 \bullet E2_{NG}}$

where,

EM_{SC} = total H_2SO_4 *manufactured* from combustion, lbs/yr

K = Molecular weight and units conversion constant
= 98.07 / 64.04 • 2000 = 3,063

98.07 = Molecular weight of H_2SO_4

64.04 = Molecular weight of SO_2

Conversion from tons per year to pounds per year – multiply by 2000.

F1 = Fuel Impact Factor for NG

$E2_{NG}$ = Sulfur dioxide (SO_2) emissions either: (1) recorded by a continuous emissions monitor, tons/yr, or (2) calculated from fuel burn data, tons/yr.

SO_2 emissions can be obtained through a calculation using the heat input of natural gas.

Equation 6-2a $\mathbf{E2_{NG} = K_b \bullet B_{NG} \bullet S}$

where,

$E2_{NG}$ = Total SO_2 production from NG combustion, tons/yr

K_b = Molecular weight and units conversion constant = 0.0001359

B_{NG} = Burn of NG in TBtu/yr

S = Sulfur content of natural gas, in grains per million standard cubic feet (Mscf), typically 2000 gr/10^6 scf per EPA AP-42.

The derivation of constant K_b is presented in Text Box F.

Text Box F: Derivation of Molecular Weight and Units Conversion Constant, K_b

K_b is determined from the following equation.

($K_b \bullet B_{NG} \bullet S$) = tons SO_2 per yr =

B_{NG} TBtu	**S** gr S	1 scf nat gas	10^{12} Btu	lb S	1 ton S	1 ton mol S	1 ton mole SO_2	64 tons SO_2
Year	10^6 scf nat gas	1050 Btu	TBtu	7000 gr S	2000 lbs S	32 tons S	1 ton mol S	1 ton mole SO_2

Grouping terms,

$= (B_{NG} \bullet S) \bullet 64 / (1050 \bullet 32 \bullet 14) = (B_{NG} \bullet S) \bullet 0.0001359$

Therefore, the value of K_b is equal to 0.0001359 tons SO_2/(TBtu • grains S/million SCF NG).

The SO_2 emissions can also be calculated from the volume of natural gas burned:

Equation 6-2b $\mathbf{E2_{NG} = K_{NG} \bullet N1 \bullet S}$

where,

$E2_{NG}$ = total SO_2 production from NG combustion, tons/yr

K_{NG} = Molecular weight and units conversion constant = $1.427 \bullet 10^{-7}$

N1 = NG burn in million standard cubic feet (Mscf) per year

S = NG sulfur content in grains per million standard cubic feet, use EPA's value of 2000 gr/10^6 scf as default

The derivation of constant K_{NG} is presented in Text Box G.

Text Box G: Derivation of Molecular Weight and Units Conversion Constant, K_{NG}

$(K_{NG} \bullet N1 \bullet S)$ = tons SO_2 per yr =

N1 10^6 scf	**S** gr S	lb S	1 ton S	1 ton mol S	1 ton mole SO_2	64 tons SO_2
Year	10^6 scf nat gas	7000 gr S	2000 lbs S	32 tons S	1 ton mol S	1 ton mole SO_2

Grouping terms,

$$(N1 \bullet S) \bullet 64 / (7000 \bullet 2000 \bullet 32) = (N1 \bullet S) \bullet 1.427 \bullet 10^{-7}$$

Therefore, the value of K_{NG} is equal to $1.427 \bullet 10^{-7}$ tons SO_2/(grains S)

Table 6-1 presents the F1 factors for simple cycle units as a function of stack temperature, as sulfuric acid vapor is related to the temperature of the exhaust. As simple cycle combustion turbines (CT) exhaust is usually around 1000°F, and TRI rules require the reporting of sulfuric acid (not of SO_3), the amount manufactured and released depends on stack temperature. Table 6-1 combines the temperature-based SO_3 to H_2SO_4 conversion with the SO_2 to SO_3 conversion to give the Fuel Impact Factor, F1.

Table 6-1
F1 – Fuel Factors for a Simple CT

Stack T, °F	F1
300	0.055
400	0.055
500	0.047
600	0.022
700	0.0055
750	0.0027
800	0.0013
850	0.00071
900	0.00039
950	0.00022
1000	0.00013
1050	0.00008
1100	0.00005
1150	0.00003
1200	0.00002

Combined Cycle Units

Sulfuric Acid Manufactured

For the case of combined cycle units, the *manufacture* of sulfuric acid is due to both combustion and SCR NOx control.

For combustion, the manufacture of sulfuric acid for combined-cycle units is described by Equation 6-3.

Equation 6-3 $$EM_{CCcom} = K \bullet F1 \bullet E2_{NG}$$

where,

EM_{CCcom}= Total H_2SO_4 *released* from combustion, lbs/yr

K = Molecular weight and units conversion constant = 98.07/64.04 • 2000 = 3,063

98.07 = Molecular weight of H_2SO_4;

64.04 = Molecular weight of SO_2;

Conversion from tons per year to pounds per year – multiply by 2000.

F1= Fuel Impact Factor for NG (See Table 6-1)

$E2_{NG}$= Sulfur dioxide (SO_2) emissions either: (1) recorded by a continuous emissions monitor, tons/yr, or (2) calculated from fuel burn data, tons/yr.

Equation 6-4 describes the manufacture of sulfuric acid in an SCR. For the case of combined cycle combustion turbines, the SCR catalyst SO_2 oxidation rate (S2) will be approximately 0.03. A more precise value can be obtained from either field test reports of SO_2 oxidation, or from the vendor's specification of the SCR catalyst or process. The Technology Impact Factor for SCR, $F3_{SCR}$, will be 1.0.

Equation 6-4 $$EM_{CCSCR} = K \bullet S2 \bullet f_{sops} \bullet E2 \bullet F3_{SCR}$$

where,

EM_{CCSCR} =Total H_2SO_4 manufactured from SCR, lbs per year

K = Molecular weight and units conversion constant = 98.07/64.04 • 2000 = 3,063

98.07 = Molecular weight of H_2SO_4;

64.04 = Molecular weight of SO_2;

Conversion from tons per year to pounds per year – multiply by 2000

S2 = SCR catalyst SO_2 oxidation rate (specified as a decimal, typically from 0.001- 0.03)

f_{sops} = Operating factor of SCR system, or the fraction of coal burn when the flue gas is directed through the SCR, whether NH_3 reagent is injected to derive

NOx reduction or not. This value should reflect the hours the SCR reactor processed flue gas, which will be site-specific but can be approximated by generally 0.8 for year-round peaking operation, 0.98 for year-round base-loaded operation, or 0.43 for seasonal operation

E2 = SO_2 produced, tons per year

$F3_{SCR}$ = Technology Impact Factor, for SCR

The total sulfuric acid *manufacture* (TSAM) for a combined cycle unit is estimated using the equation below:

Equation 6-5 $$\mathbf{TSAM = EM_{CCcom} + EM_{CCSCR}}$$

Sulfuric Acid Released

The sulfuric acid released by combustion in combined cycle units is estimated as follows:

Equation 6-6 $$\mathbf{ER_{CCcom} = EM_{CCcom} \bullet F2_{CC}}$$

where,

ER_{CCcom} = Total H_2SO_4 *released* from combustion, lbs/yr

$F2_{CC}$ = Technology Impact Factor for the combined cycle heat exchanger, equal to a value of 0.5

The equation describing the sulfuric acid release from SCR equipment on combined cycle units is estimated using a relationship similar to Equation 4-7, as follows:

Equation 6-7 $$\mathbf{ER_{CCSCR} = [EM_{CCSCR} - (K_s \bullet B \bullet f_{sreagent} \bullet S_{NH3})] \bullet F2_{cc}}$$

where,

ER_{CCSCR} = Total H_2SO_4 released from SCR, lbs per year

EM_{CCSCR} = Total H_2SO_4 manufactured from SCR, lbs per year

K_s = Conversion factor = 3799 (see Text Box C)

B = Fuel burn in TBtu/yr

$f_{sreagent}$ = Fraction of SCR operation with reagent injection, when residual NH_3 is produced that will remove SO_3.

S_{NH3} = NH_3 slip from SCR, ppmv at 6% O_2, wet (averages 0.75 ppmv over catalyst guarantee period. Actual NH_3 slip data should be used if available)

$F2_{CC}$ = Technology Impact Factor for the combined cycle heat exchanger, equal to a value of 0.5.

The total *release* of sulfuric acid from combined cycle units is then described by Equation 6-8, summing the sulfuric acid released by both combustion and SCR:

Equation 6-8 $$\mathbf{TSAR = ER_{CCcom} + ER_{CCSCR}}$$

Example 7 of Appendix A illustrates a gas-fired combined cycle plant calculation.

7

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A

EXAMPLE CALCULATIONS

Example 1: Conventional Coal-Fired Boiler with an ESP

A 500 MW pulverized coal-fired (PC) boiler, equipped with a cold-side electrostatic precipitator, burns an Eastern bituminous coal. The coal used in the reporting year is 1,126,938 tons with a weighted average sulfur concentration of 2.0% and a heating value of 12,000 Btu/lb.

Solution

Manufactured

$$E2 = K1 \bullet K2 \bullet C1 \bullet S1$$

$$E2 = 0.02 \bullet 0.95 \bullet 1{,}126{,}938 \bullet 2.0 = 42{,}824 \text{ tons } SO_2\text{/yr}$$

$$EM_{Comb} = K \bullet F1 \bullet E2$$

$$F1_{eastbit} = 1.1163E\text{-}6 \bullet SO2 + 0.0064876$$

$$SO2 = S1 \bullet \frac{K_{F1}}{HV} = 2.0 \bullet \frac{10{,}003{,}602}{12{,}000} = 1667 \text{ ppm}$$

$$F1_{eastbit} = 1.1163E\text{-}6 \bullet 1667 + 0.0064876 = 0.0083$$

$$EM_{Comb} = 3063 \bullet 0.0083 \bullet 42{,}824 = 1{,}088{,}710 \text{ lbs } H_2SO_4\text{/yr}$$

The 25,000 lbs/yr threshold has been exceeded; therefore, a release estimate must be made and the result reported on Form R.

Released

$$ER_{comb} = K \bullet F1 \bullet F2 \bullet E2$$

$$ER_{comb} = 3063 \bullet 0.0083 \bullet (0.50 \bullet 0.63) \bullet 42{,}824 = 342{,}943 \text{ lbs } H_2SO_4\text{/yr}$$

Where F2 = Air Heater • Cold-Side ESP

$$F2 = 0.50 \bullet 0.63 = 0.\ 315$$

Example 2: SCR Added to Example 1

A 500 MW PC boiler, equipped with a cold-side electrostatic precipitator, burns an Eastern bituminous coal. The plant is equipped with an SCR process that operates during the ozone season only, so that 0.43 of the coal burn occurred with the SCR operating. The SCR catalyst SO_2 oxidation rate specified in the design is 0.75%, and the ammonia slip is estimated to be 0.75

ppmv. The coal used in the reporting year is 1,126,938 tons with a weighted average sulfur concentration of 2.0% and a heating value of 12,000 Btu/lb.

Solution

Manufactured

$$E2 = K1 \bullet K2 \bullet C1 \bullet S1$$

$$E2 = 0.02 \bullet 0.95 \bullet 1{,}126{,}938 \bullet 2.0 = 42{,}824 \text{ tons } SO_2\text{/yr}$$

<u>Combustion</u>

$$EM_{comb} = K \bullet F1 \bullet E2$$

$$F1_{eastbit} = 1.1163E\text{-}6 \bullet SO2 + 0.0064877$$

$$SO2 = S1 \bullet \frac{K_{F1}}{HV} = 2.0 \bullet \frac{10{,}003{,}602}{12{,}000} = 1667 \text{ ppm}$$

$$F1_{eastbit} = 1.1163E\text{-}6 \bullet 1667 + 0.0064877 = 0.0083$$

$$EM_{Comb} = 3063 \bullet 0.0083 \bullet 42{,}824 = 1{,}088{,}710 \text{ lbs } H_2SO_4\text{/yr}$$

<u>SCR</u>

$$EM_{SCR} = K \bullet S2 \bullet f_s \bullet E2$$

$$EM_{SCR} = 3063 \bullet 0.0075 \bullet 0.43 \bullet 42{,}824 = 423{,}023 \text{ lbs } H_2SO_4\text{/yr}$$

<u>Total</u>

$$TSAM = EM_{comb} + EM_{SCR}$$

$$TSAM = 1{,}088{,}710 + 423{,}023 \text{ lbs } H_2SO_4\text{/yr}$$

$$TSAM = 1{,}511{,}733 \text{ lbs } H_2SO_4\text{/yr}$$

The 25,000 lbs/yr threshold has been exceeded; therefore, a release estimate must be made and the result reported on Form R.

Released

<u>Combustion</u>

$$ER_{Comb} = K \bullet F1 \bullet F2 \bullet E2$$

$$ER_{Comb} = 3063 \bullet 0.0083 \bullet (0.50 \bullet 0.63) \bullet 42{,}824 = 342{,}943 \text{ lbs } H_2SO_4\text{/yr}$$

Where F2 = Air Heater • Cold-Side ESP

$$F2 = 0.50 \bullet 0.63 = 0.315$$

SCR

$B = 1{,}126{,}938 \text{ tons/yr} \bullet 2000 \text{ lbs/ton} \bullet 12{,}000 \text{ Btu/lb} \bullet 1 \text{ TBtu}/10^{12} \text{ Btu}$

$B = 27.05 \text{ TBtu/yr}$

$ER_{SCR} = [EM_{SCR} - (K_s \bullet B \bullet f_s \bullet S_{NH3})] \bullet F2 \bullet F2$

$ER_{SCR} = [423{,}023 - (3799 \bullet 27.05 \bullet 0.43 \bullet 0.75)] \bullet 0.50 \bullet 0.63$

$ER_{SCR} = 122{,}812 \text{ lbs } H_2SO_4\text{/yr}$

Total

$TSAR = ER_{comb} + ER_{SCR}$

$TSAR = 342{,}943 + 122{,}812 \text{ lbs } H_2SO_4\text{/yr}$

$TSAR = 465{,}755 \text{ lbs } H_2SO_4\text{/yr}$

Example 3: Alkali Injection Added to Example 1

A 500 MW PC boiler, equipped with a cold-side electrostatic precipitator, burns an Eastern bituminous coal. The plant employs injection of alkali material (e.g., lime, sodium bicarbonate, sodium bisulfate, etc.) to control SO_3 emissions at the stack. The plant operator has conducted a series of field tests to determine the amount of alkali material that must be injected to limit flue gas SO_3 concentration at the stack. The test contractor has issued a report defining the amount of alkali that should be added to limit the stack SO_3 to 5 ppm, as measured in the flue gas at 6.6% O_2, and 8.8% moisture. The alkali injection system will be operated throughout the entire year, so that no more than 5 ppm of SO_3 at the stated conditions of excess O_2 and moisture exist in the stack.

The coal burn rate in the reporting year is 1,126,938 tons, with a weighted average sulfur concentration of 2.0%, and a heating value of 12,000 Btu/lb.

The calculation of manufactured sulfuric acid is the same as Example 1, and is repeated here:

Solution

Manufactured

$E2 = K1 \bullet K2 \bullet C1 \bullet S1$

$E2 = 0.02 \bullet 0.95 \bullet 1{,}126{,}938 \bullet 2.0 = 42{,}824 \text{ tons } SO_2\text{/yr}$

Combustion

$EM_{comb} = K \bullet F1 \bullet E2$

$F1_{eastbit} = 1.1163E\text{-}6 \bullet SO2 + 0.0064877$

$$SO2 = S1 \bullet \frac{K_{F1}}{HV} = 2.0 \bullet \frac{10{,}003{,}602}{12{,}000} = 1667 \text{ ppm}$$

$F1_{eastbit}$ = 1.1163E-6 • 1667 + 0.0064877 = 0.0083

EM_{Comb} = 3063 • 0.0083 • 42,824 = 1,088,710 lbs H_2SO_4/yr

<u>SCR</u>

EM_{SCR} = K • S2 • f_s • E2

EM_{SCR} = 3063 • 0.0075 • 0.43 • 42,824 = 423,023 lbs H_2SO_4/yr

<u>Total</u>

TSAM = EM_{comb} + EM_{SCR}

TSAM = 1,088,710 + 423,023 lbs H_2SO_4/yr

TSAM = 1,511,733 lbs H_2SO_4/yr

The 25,000 lbs/yr threshold has been exceeded; therefore, a release estimate must be made and the result reported on Form R.

Released

The total sulfuric acid released is based on the maximum value allowed by alkali injection, as measured in the stack, and the volume flow rate of combustion products processed.

The concentration of SO_3 measured at the stack can be converted to a mass emission rate, as described by Equation 4-15

$ER_{ALKINJ} = K_{alkali} \bullet B \bullet S_{SO3} \bullet F_{alkali} \bullet F2_x$

where,

ER_{ALKINJ} = Total H_2SO_4 released from unit equipped with alkali injection, lbs per year

K_{alkali} = Constant, equal to 3,799, with units of lbs H_2SO_4/(TBtu ppmv SO_3) (SO_3 measured at @ 6% O_2 and 8.1% H_2O)

B = 27.05 TBtu/yr, for the specific case of Example 1

S_{SO3} = SO_3 content as measured in the stack or particulate collector exit, corrected to a concentration basis of ppmv at 6% O_2, 8.1% moisture

F_{alkali} = fraction of operation with alkali addition to remove SO_3.

$F2_x$ = 1 (as the SO_3 measurement is in the stack, there are no control technology components downstream of the measurement)

The conversion factor K_{alkali} is equal to 3,799 (see Text Box C). This constant is derived for the case where flue gas SO_3 is reported in terms of 6% oxygen and wet flue gas at 8.1% H_2O.

However, the SO_3 concentration of 5 ppm in the stack is measured at slightly different conditions of excess O_2 and moisture (6.6% oxygen and 8.8% moisture and therefore, a new value of K_{alkali} must be calculated:

K_{alkali} (O_2, H_2O) = 3799 (6% O_2, 8.1% H_2O) • [(100-8.1)/(100-new H_2O)] • [(20.9 – 6.0)/(20.9 – new O_2)]

K_{alkali} (O_2, H_2O) = 3799 (6% O_2, 8.1% H_2O) • [(100-8.1)/(100-8.8)] • [(20.9 – 6.0)/(20.9 – 6.6)]

K_{alkali} (6.6%, 8.8%) = 3799 • [1.0077)• [1.034]

K_{alkali} (6.6%, 8.8%) =3958

Total sulfuric acid release is then calculated as follows:

ER_{ALKINJ} = [3,958] • [27.05] •[5.0] • [1] • [1]

ER_{ALKINJ} = 535,320 lbs/yr

TSAR = ER_{ALKINJ}

TSAR = 535,320 lbs/yr

Example 4: 500 MW PRB-fired Boiler with ESP, SCR

A 500 MW PC boiler, equipped with a cold-side electrostatic precipitator, burns a PRB coal. The plant is equipped with an SCR process that operates during the ozone season only, so that 0.43 of the coal burn occurred with the SCR operating. The SCR catalyst SO_2 oxidation rate specified in the design is 2%, and the ammonia slip is estimated to be 0.75 ppmv. The coal used in the reporting year is 1,384,552 tons with a weighted average sulfur concentration of 0.40% and a heating value of 8,500 Btu/lb.

Solution

Manufactured

E2 = K1 • K2 • C1 • S1

E2 = 0.02 • 0.875 • 1,384,552 • 0.40 = 9,692 tons SO_2/yr

Combustion

EM_{comb} = K • F1 • E2

EM_{comb} = 3063 • 0.0019 • 9,692 = 56,404 lbs H_2SO_4/yr

SCR

EM_{SCR} = K • S2 • f_s • f_{3SCR} • E2

EM_{SCR} = 3063 • 0.020 • 0.43 • 0.17 • 9,692 = 43,402 lbs H_2SO_4/yr

Total

$TSAM = EM_{comb} + EM_{SCR}$

$TSAM = 56{,}404 + 43{,}402$ lbs H_2SO_4/yr

$TSAM = 99{,}806$ lbs H_2SO_4/yr

The 25,000 lbs/yr threshold has been exceeded; therefore, a release estimate must be made and the result reported on Form R.

Released

Combustion

$ER_{Comb} = K \bullet F1 \bullet F2 \bullet E2$

$ER_{Comb} = 3063 \bullet 0.0019 \bullet (0.36 \bullet 0.72) \bullet 9{,}692 = 14{,}620$ lbs H_2SO_4/yr

Where F2 = Air Heater • Cold-Side ESP

$F2 = 0.36 \bullet 0.72 = 0.26$

SCR

B = 1,384,552 tons/yr • 2000 lbs/ton • 8,500 Btu/lb • 1 TBtu/10^{12} Btu

B =23.54 TBtu/yr

$ER_{SCR} = [EM_{SCR} – (K_s \bullet B \bullet f_s \bullet S_{NH3})] \bullet F2 \bullet F2$

$ER_{SCR} = [43{,}402 – (3799 \bullet 23.54 \bullet 0.43 \bullet 0.75)] \bullet 0.36 \bullet 0.72$

$ER_{SCR} = 3{,}774$ lbs H_2SO_4/yr

Total

$TSAR = ER_{comb} + ER_{SCR}$

$TSAR = 14{,}620 + 3{,}774$ lbs H_2SO_4/yr

$TSAR = 18{,}394$ lbs H_2SO_4/yr

Example 5: FGC Added to Example 1

A 500 MW PC boiler, equipped with a cold-side electrostatic precipitator, burns an Eastern bituminous coal. The plant is equipped with a FGC process that injects both SO_3 and NH_3, with the SO_3 injected upstream of the air preheater. The SO_3 is injected at 7 ppmv at 6% O_2 wet, and the ammonia at 3 ppmv also at 6% O_2 wet. The FGC system operates whenever the plant is on, except during startup and shutdown, with an operating factor estimated at 0.9. The coal used in the reporting year is 1,126,938 tons with a weighted average sulfur concentration of 2.0% and a heating value of 12,000 Btu/lb.

Solution

Manufactured

$E2 = K1 \bullet K2 \bullet C1 \bullet S1$

$E2 = 0.02 \bullet 0.95 \bullet 1{,}126{,}938 \bullet 2.0 = 42{,}824$ tons SO_2/yr

Combustion

$EM_{Comb} = K \bullet F1 \bullet E2$

$F1_{eastbit} = 1.1163E\text{-}6 \bullet SO2 + 0.0064877$

$$SO2 = S1 \bullet \frac{K_{F1}}{HV} = 2.0 \bullet \frac{10{,}003{,}602}{12{,}000} = 1667 \text{ ppm}$$

$F1_{eastbit} = 1.1163E\text{-}6 \bullet 1667 + 0.0064877 = 0.0083$

$EM_{Comb} = 3063 \bullet 0.0083 \bullet 42{,}824 = 1{,}088{,}710$ lbs H_2SO_4/yr

FGC

$B = 1{,}126{,}938$ tons/yr $\bullet$ 2000 lbs/ton $\bullet$ 12000 Btu/lb $\bullet$ 1 TBtu/10^{12} Btu

$B = 27.05$ TBtu/yr

$EM_{FGC} = K_e \bullet B \bullet f_e \bullet I_s$

$EM_{FGC} = 3799 \bullet 27.05 \bullet 0.9 \bullet 7 = 647{,}407$ lbs H_2SO_4/yr

Total

$TSAM = EM_{Comb} + EM_{FGC}$

$TSAM = 1{,}088{,}710 + 647{,}407$ lbs H_2SO_4/yr

$TSAM = 1{,}736{,}117$ lbs H_2SO_4/yr

The 25,000 lbs/yr threshold has been exceeded; therefore, a release estimate must be made and the result reported on Form R.

Released

Combustion

$ER_{Comb} = K \bullet F1 \bullet F2 \bullet E2$

$ER_{Comb} = 3063 \bullet 0.0083 \bullet (0.50 \bullet 0.63) \bullet 42{,}824 = 342{,}943$ lbs H_2SO_4/yr

Where F2 = Air Heater $\bullet$ Cold-Side ESP

$F2 = 0.50 \bullet 0.63 = 0.315$

FGC

$B = 1{,}126{,}938 \text{ tons/yr} \bullet 2000 \text{ lbs/ton} \bullet 12000 \text{ Btu/lb} \bullet 1 \text{ TBtu}/10^{12} \text{ Btu}$

$B = 27.05 \text{ TBtu/yr}$

$ER_{FGC} = [EM_{FGC} - (K_e \bullet B \bullet f_e \bullet I_{NH3})] \bullet F3 \bullet F2$

$ER_{FGC} = [647{,}407 - (3799 \bullet 27.05 \bullet 0.9 \bullet 3.0)] \bullet 0.25 \bullet 1.0$

$ER_{FGC} = 92{,}487 \text{ lbs } H_2SO_4\text{/yr}$

Since there are no other control devices after the ESP, then F2 = 1.0.

Total

$ESAR = ER_{Comb} + ER_{FGC}$

$ESAR = 342{,}943 + 92{,}487 \text{ lbs } H_2SO_4\text{/yr}$

$ESAR = 435{,}430 \text{ lbs } H_2SO_4\text{/yr}$

Example 6: SCR and FGC Added to Example 1

A 500 MW PC boiler, equipped with a cold-side electrostatic precipitator, burns an Eastern bituminous coal. The plant is equipped with an SCR process that operates during the ozone season only, so that 0.43 of the coal burn occurred with the SCR operating. The SCR catalyst SO_2 oxidation rate specified in the design is 0.75%, and the ammonia slip is estimated to be 0.75 ppmv. The plant is also equipped with a FGC process that injects both SO_3 and NH_3, with the SO_3 injected upstream of the air preheater. The SO_3 is injected at 7 ppmv at 6% O_2 wet, and the ammonia at 3 ppmv also at 6% O_2 wet. The FGC system operates whenever the plant is on, except during startup and shutdown, with an operating factor estimated at 0.9. The coal used in the reporting year is 1,126,938 tons with a weighted average sulfur concentration of 2.0% and a heating value of 12,000 Btu/lb.

Solution

From previous examples:

Manufactured

Total

$TSAM = EM_{Comb} + EM_{SCR} + EM_{FGC}$

$TSAM= 1{,}088{,}711 + 423{,}023 + 647{,}407 \text{ lbs } H_2SO_4\text{/yr}$

$TSAM = 2{,}159{,}141 \text{ lbs } H_2SO_4\text{/yr}$

The 25,000 lbs/yr threshold has been exceeded; therefore, a release estimate must be made and the result reported on Form R.

Released

Combustion

ER_{Comb} = K • F1 • F2 • E2

ER_{Comb} = 3063 • 0.0083 • (0.50 • 0.63) • 42,824 = 342,943 lbs H_2SO_4/yr

SCR

ER_{SCR} = [EM_{SCR} – (K_s • B • f_s • S_{NH3})] • F2 • F2

ER_{SCR} = [423,023 – (3799 • 27.05 • 0.43 • 0.75)] • 0.50 • 0.63

ER_{SCR} = 122,812 lbs H_2SO_4/yr

FGC

ER_{FGC} = [EM_{FGC} – (K_E • B • f_E • I_{NH3})] • F3 • F2

ER_{FGC} = [647,407 – (3799 • 27.05 • 0.9 • 3.0)] • 0.25 • 1.0

ER_{FGC} = 92,487 lbs H_2SO_4/yr

Total

TSAR = ER_{Comb} + ER_{SCR} + ER_{FGC}

TSAR = 342,943 + 122,812 + 92,487 lbs H_2SO_4/yr

TSAR = 558,242 lbs H_2SO_4/yr

Example 7: Coal-Fired Boiler with FGC, NG Startup Fuel, and Used Oil Co-Firing

A 500 MW PC boiler, equipped with a cold-side electrostatic precipitator, burns an Eastern bituminous coal as the main fuel. The plant is equipped with an SCR process that operates during the ozone season only, so that 0.43 of the coal burn occurred with the SCR operating. The ammonia slip is estimated to be 0.75 ppmv. The plant is also equipped with a FGC process that injects both SO_3 and NH_3, with the SO_3 injected upstream of the air preheater. The SO_3 is injected at 7 ppmv at 6% O_2 wet, and the ammonia at 3 ppmv also at 6% O_2 wet. The FGC system operates whenever the plant is on, except during startup and shutdown, with an operating factor estimated at 0.9. The coal used in the reporting year is 1,126,938 tons with a weighted average sulfur concentration of 2.0% and a heating value of 12,000 Btu/lb. Natural gas is used as a startup fuel, with 0.5 TBtu per year. During startup, neither the SCR nor the FGC system is used. Used oil is also burned, with 483.2 tons burned (0.0185 TBtu/yr) in the year. Since the used oil is burned when the unit is at full load, it is burned while the SCR and FGC are both operating. The used oil has a sulfur content of 0.1% from analysis.

Solution

Coal fuel calculations

*Manufacture*d from coal, from previous examples

Total

$TSAM = EM_{Comb} + EM_{SCR} + EM_{FGC}$

$TSAM = 1,088,711 + 423,023 + 647,407$ lbs H_2SO_4/yr

$TSAM = 2,159,141$ lbs H_2SO_4/yr

Released from coal, from previous examples

Total

$TSAR = ER_{Comb} + ER_{SCR} + ER_{FGC}$

$TSAR = 342,943 + 122,812 + 92,487$ lbs H_2SO_4/yr

$TSAR = 558,242$ lbs H_2SO_4/yr

Natural gas fuel calculations

Manufactured from natural gas

Combustion

$E2_{NG} = K_b \bullet B_{NG} \bullet S$

$E2_{NG} = 0.0001359 \bullet 0.5$ TBtu/yr $\bullet$ 2000 gr/10^6 scf

$E2_{NG} = 0.136$ tons SO_2/year

$EM_{Comb} = K \bullet F1 \bullet E2_{NG}$

$EM_{Comb} = 3063 \bullet 0.01 \bullet 0.136$

$EM_{Comb} = 4.16$ lbs H_2SO_4 manufactured

No sulfuric acid is manufactured in either the SCR or FGC.

Released from natural gas

Combustion

$ER_{Comb} = K \bullet F1 \bullet F2 \bullet E2_{NG}$

$ER_{Comb} = 3063 \bullet 0.01 \bullet 0.50 \bullet 0.63 \bullet 0.136$

$ER_{Comb} = 1.31$ lbs H_2SO_4 released

F2 is taken to be equal to 0.50 for the air heater and 0.63 for the ESP.

Used oil fuel calculations

Manufactured from used oil

Combustion

$E2 = K1 \bullet K2 \bullet C1 \bullet S1$

$E2 = 0.02 \bullet 1.0 \bullet 483.2 \bullet 0.1$

$E2 = 0.966$ tons SO_2/year

$EM_{Comb} = K \bullet F1 \bullet E2$

$EM_{Comb} = 3063 \bullet 0.0175 \bullet 0.966$

$EM_{Comb} = 51.8$ lbs H_2SO_4 manufactured

SCR

$EM_{SCR} = K \bullet S2 \bullet f_s \bullet E2$

$EM_{SCR} = 3063 \bullet 0.0075 \bullet 1.0 \bullet 0.966$

$EM_{SCR} = 22.2$ lbs H_2SO_4 manufactured

FGC

$EM_{FGC} = K_e \bullet B \bullet f_e \bullet I_s$

$EM_{FGC} = 3799 \bullet 0.0185 \bullet 1.0 \bullet 7.0$

$EM_{FGC} = 492$ lbs H_2SO_4 manufactured

Total

$TSAM = EM_{Comb} + EM_{SCR} + EM_{FGC}$

$TSAM = 51.8 + 22.2 + 492$ lbs H_2SO_4/yr

$TSAM = 566$ lbs H_2SO_4/yr

Released from used oil

Combustion

$ER_{Comb} = K \bullet F1 \bullet F2 \bullet E2$

$ER_{Comb} = 3063 \bullet 0.0175 \bullet 0.50 \bullet 0.63 \bullet 0.966$

$ER_{Comb} = 16.3$ lbs H_2SO_4 released

SCR

$ER_{SCR} = [EM_{SCR} - (K_s \bullet B \bullet f_s \bullet S_{NH3})] \bullet F2 \bullet F2$

$ER_{SCR} = [22.2 - (3799 \bullet 0.0185 \bullet 1.0 \bullet 0.75)] \bullet 0.50 \bullet 0.63$

$ER_{SCR} = -9.6$ lbs H_2SO_4/yr

F2 is taken to be equal to 0.50 for the air heater and 0.63 for the ESP.

FGC

$ER_{FGC} = [EM_{FGC} – (K_e \bullet B \bullet f_e \bullet I_{NH3})] \bullet F3 \bullet F2$

$ER_{FGC} = [492 – (3799 \bullet 0.0185 \bullet 1.0 \bullet 3.0)] \bullet 0.25 \bullet 1.0$

ER_{FGC} = 70.3 lbs H_2SO_4/yr

Total

$TSAR = ER_{Comb} + ER_{SCR} + ER_{FGC}$

TSAR = 16.3 – 9.6 + 70.3 lbs H_2SO_4/yr

TSAR= 77 lbs H_2SO_4/yr

Grand totals for all fuels

Manufactured

$TSAM = TSAM_{coal} + TSAM_{NG} + TSAM_{oil}$

TSAM = 2,159,141 + 4.16 + 566 lbs H_2SO_4/yr

TSAM = 2,159,211 lbs H_2SO_4/yr

Released

$TSAR = TSAR_{coal} + TSAR_{NG} + TSAR_{oil}$

TSAR = 558,242 + 1.31 + 77 lbs H_2SO_4/yr

TSAR = 558,320 lbs H_2SO_4/yr

Example 8: Natural Gas Combined Cycle Plant

A natural gas-fired combined-cycle unit uses 12.3 TBtu of natural gas, with the standard sulfur content.

Solution

Manufactured

$E2_{NG} = K_b \bullet B_{NG} \bullet S = 0.0001359 \bullet 12.3 \bullet 2000 = 3.343$ tons SO_2/yr
$EM_{CC} = K \bullet F1 \bullet E2_{NG} = 3063 \bullet 0.0555 \bullet 3.343 = 568$ lbs H_2SO_4 manufactured

Released

$ER_{CC} = K \bullet F1 \bullet F2 \bullet E2_{NG} = 3063 \bullet 0.0555 \bullet 0.5 \bullet 3.343 = 284.5$ lbs H_2SO_4 released

(F2 = 0.5 because of the low temperature of the back-end tubes of the HRSG, like an air heater.)

B

CHRONOLOGY OF CHANGES TO EPRI SULFURIC ACID ESTIMATION MODEL

EPRI, 2010 (EPRI Report 1020636)

Modification	Description
Fuel Impact Factor (F1)	Combined low and high-sulfur eastern bituminous coals into a single category with a linear curve fit. F1 factor based on fuel SO_2 content calculated from fuel sulfur content: $F1_{ebit} = 1.1163E\text{-}6 \bullet SO_2 + 0.0064877$ Changed the following F1 factors based on additional data: Subbit/PRB – changed from 0.0018 to 0.0019 Lignite – changed from 0.0048 to 0.0044
Technology Factors (F2)	Changed factors for APH and ESP due to addition and re-evaluation of data: APH, low-sulfur east. bit. – changed from 0.49 to 0.50 APH, PRB – changed from 0.56 to 0.36 ESP, low-sulfur east. bit – changed from 0.49 to 0.63 ESP, PRB – changed from 0.73 to 0.72 Corrected placement of Srivastava and Buckley reference values in Figure 4-4.
Alkali Injection	Added a procedure to determine total releases from partial year injection. Incorporated correction to alkali injection conversion factor, K_{alkali}
Report Organization	Moved F2 Factors from Section 3 to Section 4
Examples	Updated examples to account for new F1 and F2 factors

EPRI, 2008 (EPRI Report 1016384)

Modification	Description
Alkali Injection	Added a procedure to estimate a stack release using a measured or specified stack gas SO_3 concentration, to support estimates on units with alkali injection. Errata page published to correct error in alkali injection conversion factor, K_{alkali}

Combustion Turbines	Clarified procedures for estimating emissions from simple and combined cycle CTs.
Blended Coals	New method calculates SO_3 manufacture by calculating the SO_3 emission rate separately for each of the component coals, and proportioning the contribution of SO_3 from each. The prior method assumed the SO_3 production was the same as that of the major coal component.
Examples	Provided new example calculations for alkali injection and blended coal.

EPRI, 2007 (Report 1014773) changes from Harrison, 2005.

Modification	**Description**
Formatting	Adapted Southern Company paper (Harrison, 2005) to EPRI format.
Fuel (F1) Factors	Changed the following F1 factors based on additional data: Low S E. Bit, Dry Boiler – from 0.0080 to 0.0082 Subbit. (including PRB), Dry Boiler – from 0.0014 to 0.0018 Subbit. (including PRB), Cyclone – from 0.003 to 0.0018
Technology (F2) Factors	Added new F2 Factors: Air Preheater, PRB fuel - 0.56 Cold-side ESP, PRB fuel – 0.73
SCR	Added a Technology Impact Factor for SCR, $F3_{SCR}$

1020636

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