ENVIRONMENTAL, HEALTH AND SAFETY ASSESSMENT APPLICATION OF A HEAT INTEGRATED, POST-COMBUSTION CO_2 CAPTURE SYSTEM USING MONOETHANOLAMINE AND HITACHI H3-1 SOLVENT AT THE E. W. BROWN COAL-FIRED POWER PLANT HARRODSBURG, KENTUCKY

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DISCLAIMER

ABSTRACT

An Environmental Health and Safety (EH&S) Assessment was completed for operation of a pilot scale carbon dioxide (CO_2) capture system (CCS) at the Louisville Gas & Electric (LG&E) and Kentucky Utilities (KU) Energy, LLC (LG&E-KU) E. W. Brown Generating Station in Harrodsburg, Mercer County, Kentucky. The pilot system was evaluated using two CO_2 capture solvents, monoethanolamine (MEA) and Hitachi's H3-1 solvent.

The purpose of the EH&S Assessment was to determine if there were any unacceptable environmental, health or safety concerns that may prevent operation or environmental permitting of a larger scale pilot scale plant. The assessment included review of process flow diagrams, input and output flow rates for primary materials, literature describing similar processes and chemicals used or created during the process, actual air emission and wastewater test data and air emission calculations. The evaluation included identification of risks related to hazardous chemicals, air emissions, wastewater discharges, solid wastes generated and employee hazards.

Most potential EH&S issues that were identified are commonly found and successfully managed at large industrial facilities. No risks were identified that could not be successfully managed or would likely prevent implementation or environmental permitting of the pilot or larger scale plant. Potential exposures and resulting health risks from exposure to low concentrations of nitrosamines generated from degradation of the Hitachi H3-1 and possibly MEA solvents may be a health concern for site workers, but additional investigation is needed to accurately assess this risk.

Applying the information gained from operating the pilot plant, performing air emission testing and used solvent testing to a large-scale facility at a commercial coal-fired electric generating plant suggests additional air emission control measures may be necessary to reduce potential site worker health risks and possibly community risks. Depending upon the location and regional air quality, considerable effort may be required to obtain the necessary air permit for construction and operation of a similarly configured large-scale PCCCS facility.

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LIST OF ACRONYMS AND ABBREVIATIONS

ACFM	Actual Cubic Feet per Minute
ACGIH	American Conference of Governmental Industrial Hygienists
AMP	Aminomethylpropanol
BACT	Best Available Control Technology
CAA	Clean Air Act
CAP	Criteria Air Pollutant
CFR	U.S. Code of Federal Regulations
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COC	Constituent of Concern
CCS	Carbon Capture System
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DOE/NETL	U.S. Department of Energy, National Energy Technology Laboratory
EHS	Extremely Hazardous Substances
EH&S	Environmental Health & Safety
EPC	Exposure Point Concentration
EPCRA	Emergency Planning and Community Right to Know Act
EPRI	Electric Power Research Institute
HAP	Hazardous Air Pollutant
HMIS	Hazardous Materials Identification System
IARC	International Agency for Research on Cancer
IRIS	USEPA Integrated Risk Information System
KAR	Kentucky Administrative Regulation
KPDES	Kentucky Pollutant Discharge Elimination System
kg	Kilogram
kg/d	Kilogram per day
KYERC	Kentucky Emergency Response Commission
KU	Kentucky Utilities
LAER	Lowest Achievable Emission Rate
LEPC	Local Emergency Planning Committee
LG&E	Louisville Gas & Electric
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
MDL	Method Detection Limit
mg/L	Milligram per liter
MSDS	Material Safety Data Sheet
MWe	Megawatt-electric power
MWth	Megawatt-thermal power

LIST OF ACRONYMS AND ABBREVIATIONS

μg/L	Microgram per liter
NAAQS	National Ambient Air Quality Standard
NA-NSR	Nonattainment New Source Review
NILU	Norwegian Institute for Air Research
NIOSH	National Institute for Occupational Safety and Health
NO_X	Nitrogen Oxides
NTP	U.S. Department of Health and Human Services National Toxicology Program
NSPS	New Source Performance Standard
NSR	New Source Review
OSHA	U.S. Occupational Safety and Health Administration
PANNA	Pesticide Action Network North America
PCCCS	Post-Combustion CO_2 Capture System
PEL	Permissible Exposure Limit
PM_{10}	Particulate Matter less than 10 micrometers in diameter
PSD	Prevention of Significant Deterioration
PTE	Potential-to-Emit
R&D	Research and Development
RAP	Regulated Air Pollutant
RCRA	Resource Conservation and Recovery Act
REL	Recommended Exposure Limit
RSL	Regional Screening Level
SCMH	Standard Cubic Meters per Hour
SER	Significant Emission Rate
SO_2	Sulfur Dioxide
STEL	Short-term Exposure Level
TLV	Threshold Limit Value
UKy-CAER	University of Kentucky Center for Applied Energy Research
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WFGD	Wet Flue Gas Desulfurization Unit

EXECUTIVE SUMMARY

This EH&S assessment was conducted to evaluate a pilot-scale, post-combustion CO_2 capture system (PCCCS) installed at the E.W. Brown coal-fired electric generating plant in Harrodsburg, Kentucky. The assessment was funded by a grant from the U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL) (Project Number DE-FE0007395).

The objective was to determine if there were any unacceptable environmental, health or safety concerns that may prevent implementation or environmental permitting of similar pilot scale plants and to evaluate potential ramifications of a larger scale (500 MWe) PCCCS. The scope of the assessment was limited to evaluating process design plans, process operation and testing information provided by the University of Kentucky Center for Applied Energy Research (UKy-CAER) and Hitachi as well as a literature review. Process design and operation information included: process flow diagrams; operating parameters; raw material storage and consumption rates; air emissions testing; solvent testing; quantification and characterization of wastes generated and wastewater discharged.

The pilot PCCCS has a two-stage stripper configuration with an optimized two-stage cooling tower concept. The PCCCS evaluated the performance of a conventional CO_2 scrubbing solvent (monoethanolamine or MEA) and the advanced Hitachi H3-1 solvent. The Hitachi solvent is proprietary and its specific formulation was not available. Information provided by Hitachi identified the solvent as a mixture of water and an amine based solvent with properties similar to MEA. A MSDS provided by Hitachi indicated the solvent had no carcinogens listed by common public sources and it had no constituents identified on USEPA's *Consolidated List of Chemicals Subject to the Emergency Planning and Community Right to Know Act (EPCRA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Section 112 (r) of the Clean Air Act* (CAA).

Direct contact with MEA and H3-1 were the primary employee health hazards from raw material handling, since both are identified as corrosive and irritants in concentrated form. These hazards are readily mitigated by avoiding exposure to the capture solvents by using appropriate PPE. Similarly, safety hazards that included potential exposure to noise, heat, steam and pressure vessels were not unusual for an industrial facility and managed with appropriate precautions and PPE to avoid accidents and injuries.

Using MEA as the capture solvent, the maximum detected air emission concentration for ammonia at the primary absorber and secondary stripper exhausts exceeded the USEPA Regional Screening Level (RSL) for air and occupational exposure thresholds (OSHA PEL and ACGIH TLV). Maximum detected air emission concentrations for MEA exceeded occupational thresholds at the primary absorber and secondary stripper. MEA concentrations at the primary absorber and secondary stripper also exceeded the ACGIH Short-term Exposure Level (STEL, 15,000 $\mu g/m^3$). Maximum detected air emission concentrations at the primary absorber for formaldehyde exceeded the USEPA RSL, but not above an occupational threshold (PEL). The maximum detected concentration of formaldehyde at the secondary stripper exceeded the USEPA RSL and both occupational exposure thresholds (PEL and TLV).

Detected concentrations exceeding occupational exposures do not necessarily indicate a cause for employee exposure concern, since employees would not be exposed to air emissions from the primary absorber and secondary stripper for 8 hours per day, 5 days per week for 30 years. Similarly, concentrations detected above USPEA RSLs do not necessarily indicate a community concern for ambient air quality due to the emissions being diluted in the exhaust stack for the generating station. However, elevated concentrations of ammonia, MEA and possibly formaldehyde detected at the secondary stripper and extrapolated to a large-scale facility warrants additional evaluation and consideration of additional emission control measures, if the exit gas stream from the secondary stripper were not directed to a boiler and used for combustion air.

Formation of nitrosamines may occur from the degradation of MEA, but were not detected in air emissions or used solvent at a concentration low enough to fully evaluate potential health effects if they were present. Nitrosamines were identified in a generic form during the use of the Hitachi H3-1 solvent. Nitrosamines are a concern since they are considered human carcinogens, even at very low levels of exposure. The degree of affect is dependent upon the specific isomer. Assessment of potential exposures to nitrosamines during the study using assumptions based upon limited data indicates that researcher exposure levels may exceed USEPA acceptable cancer risk ranges of 1E-06 to 1E-04. Additional assessment of actual exposure frequencies, durations and concentrations of specific nitrosamine isomers at lower detection levels is warranted to better characterize potential health risks.

Due to uncertainties in the exposure scenarios considered and data generated, extrapolating these results to operation of a large scale PCCCS may not accurately identify potential risks of nitrosamine exposure by site workers or the surrounding community. However, it is reasonable to presume that a larger scale facility will consume greater amounts of solvent that, depending upon the solvent formulation, may generate larger amounts of nitrosamines, albeit at similar concentrations with increased air flow, that could result in greater risk of exposure and harmful health effects without additional emission control measures.

Air emission test data and calculated potential emissions exceeded estimates determined in the Initial Environmental, Health and Safety Assessment (SMG, 2012). Although actual air emissions were higher than estimated, operation of the pilot plant for limited hours as a research and development facility would still qualify as an Insignificant Activity (IA); however, if the pilot plant were operated more than 6700 hours per year, the E.W. Brown facility may be required to modify its Title V air permit.

MEA with associated degradation compounds were the largest contributors to actual air emissions during the MEA campaign. The highest emitting degradation compound was ammonia (1.66 tons). Formaldehyde air emissions from the H3-1 campaign were considerably higher at the secondary stripper (relative to the MEA campaign results) and ammonia emissions were substantially lower at both the primary absorber and secondary stripper. Although actual air emissions were higher than estimated, the relatively small amount of emissions would not adversely impact surrounding terrestrial or water resources, since they were readily diluted and dispersed from the main exhaust stack at the E.W. Brown Generating Station.

Extrapolating data obtained from the pilot plant testing suggests that a larger scale (550 MWe) PCCCS located at an existing coal-fired steam electric plant would trigger a Prevention of Significant Deterioration (PSD) review, likely requiring installation of best available control technology (BACT) for VOC emissions. If the system were installed within a Nonattainment Area for VOCs, the project would also be subject to the Nonattainment New Source Review (NA-NSR) program that requires application of the lowest achievable emission rate (LAER) technology. BACT or LAER control measures for VOC emissions can add significant costs to the installation and operation of a 550 MWe PCCCS and the plausible permitting procedure could require a minimum of 1.5 – 2.5 years for approval prior to commencing construction.

Extrapolated air emissions from a large scale PCCCS suggest ammonia, process solvent and other solvent degradation products (e.g., acetic acid) will likely be emitted in quantities requiring emission controls. Potential emissions for solvent degradation products exceed 1,500 tons per year, with ammonia emissions being the largest component (about 1,270 tons per year). While the extrapolation methods used in this assessment are useful to estimate order-of-magnitude impacts, specific process data for: gas flow rates, solvent liquid flow rates, stack parameters (height, diameter, gas velocity), and flue gas composition are needed before accurately quantifying risks/impacts to human health or the environment.

The pilot construction area was too small to require a construction permit for storm water discharges. Depending upon the location, a larger scale facility will likely require a permit and storm water pollution plan implemented prior to construction.

Make up water required for the CO_2 absorber and pretreatment tower were minor relative to the amount of water required to operate the power station. Make up water was obtained from E.W. Brown's permitted water intake supply and no additional permitting for, or acquisition of, make up water was required. A larger scale facility will require a greater amount of water. The source of water will need to be evaluated to determine sufficient quantity and quality as well as associated environmental permitting requirements.

Process wastewater volumes were relatively minor and primarily generated from the SO_2 pretreatment tower and cooling tower blowdown. Wastewaters were pumped to a wet flue gas desulfurization (WFGD) unit on site as a supplement water source and were not discharged or disposed on site. Due to the wastewater volumes, contaminant concentrations and ultimate disposal method, wastewater management was not a significant environmental concern. Increased wastewater volumes and constituent concentrations for a larger scale facility will need further evaluation to determine appropriate disposal methods. Recent changes in steam electric power generating effluent guidelines published by the EPA (40 CFR Part 423) will need to be considered to determine any required treatment and associated implementation needs for surface water discharges.

Waste quantities and constituent concentrations estimated in the initial EHS Assessment (SMG, 2012) were generally consistent with actual wastes generated. In many cases, volume of waste was less than anticipated. A few unanticipated wastes were generated from periodic maintenance and cleaning activities that were not a hazardous waste. Unexpected, used H3-1 solvent was characterized as a hazardous waste due to selenium concentration. A larger scale facility will generate relatively greater waste volumes, although there should be some economy of scale that will prevent a directly proportional increase in waste generated. Management of a larger volume of wastes not regulated as a hazardous waste should be manageable for a typical steam electric power generating facility. Increased quantities of hazardous waste due to use of the H3-1 solvent would need to be considered in future operating plans, registered and managed appropriately.

1.0 INTRODUCTION/BACKGROUND

1.1 Project Funding and Description

This Environmental Health and Safety (EH&S) Assessment was funded by grants from the U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL Project Number DE-FE0007395), the Carbon Management Research Group (CMRG, a utility group comprised of Duke Energy, American Electric Power, East Kentucky Power, Electric Power Research Institute (EPRI) and LKE) and the Kentucky Department for Energy Development and Independence. Project partners are: UKy-CAER, EPRI and Hitachi Power Systems America. The project consists of planning, design, pilot testing and evaluation of an experimental CO_2 capture system at a coal-fired electric generating station.

1.2 Project Purpose and Objectives

The purpose of this EH&S Assessment was to identify significant environmental, health or safety risks associated with the operation of a pilot PCCCS at the coal fired E. W. Brown Generating Station at Harrodsburg, Kentucky (see **Figure 1 Site Location Map, Figure 2 Site Vicinity Map** and **Figure 3 CCS Slipstream Location**). This assessment includes information gathered during operation of the pilot plant to evaluate potential EH&S impacts and controls needed for design and implementation of a commercial-scale (550 megawatt equivalent (MWe) carbon capture plant.

The purpose of the pilot project was to test a novel heat integration scheme using waste heat from the CCS to improve the plant and system efficiency to meet DOE/NETL performance and cost targets of 90% CO_2 capture, 95% CO_2 purity and an increase in the cost of electricity of no more than 35%. This is accomplished using a two-stage stripper configuration where the second stage is designed as an air stripper to remove additional carbon loading in the lean solvent with the CO_2 laden exit air feeding into the boiler as combustion air. An optimized two-stage cooling tower concept was incorporated to reduce the condenser temperature, thereby improving the turbine efficiency (see **Figure 4 CCS Process Flow Diagram**). The purpose was also to use and evaluate the performance of MEA and Hitachi H3-1 advanced solvent in this novel carbon capture process.

1.3 EH&S Evaluation Process and Objectives

Process design and operation information was obtained from the UKy-CAER. This information included process flow diagrams, operating parameters, raw material storage and consumption with resulting estimated air emissions, wastes generated and wastewater discharges. The pilot plant was designed to operate at a 0.7 MWe (2 MWth) scale (~13.7 tonnes per day CO_2) receiving a slipstream flow of approximately 2340 SCMH (1400 cfm) from the E.W. Brown combined exhaust stream, after the WFGD. The pilot plant was approximately 24.5 meters (80 ft.) tall and had a footprint of about 93 m^2 (1000 ft^2), excluding associated lab/control center and auxiliary facilities. It operated for about 1.5 years for testing and evaluation purposes.

A literature review was performed to identify environmental, health and safety hazards of raw materials used in the process as well as information available for similar operations to evaluate potential air emissions, wastes and wastewater generated. Additionally, chemical constituent evaluation was conducted for substances known or anticipated to be generated by the process.

The Hitachi solvent is proprietary and the specific formulation was not available. According to information provided by Hitachi, the solvent is a mixture of water and an amine based solvent with EH&S properties (see **Appendix A** for MSDS) similar to MEA, a more conventional solvent used for CO_2 capture that will also be used at the pilot plant for benchmarking and performance comparison with the Hitachi solvent. From this information, the initial evaluation presumed that the Hitachi solvent would not have significantly different health or environmental hazards than MEA.

Hitachi was also consulted to determine if their solvent contained any federal, environmentally regulated constituents identified on the United States Environmental Protection Agency's (USEPA) *Consolidated List of Chemicals Subject to the Emergency Planning and Community Right to Know Act (EPCRA), Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Section 112 (r) of the Clean Air Act* (CAA) available on their web site and current as of March 2015. This list includes: EPCRA Section 302 Extremely Hazardous Substances (EHS, as identified in Title 40 of the Code of Federal Regulations (CFR) Part 355), EPCRA Section 313 Toxic Chemicals (as identified in 40 CFR Part 372), CERCLA Hazardous Substances (as identified in 40 CFR Part 302) and CAA regulated toxic and flammable substances (as identified in 40 CFR Part 68).

Hitachi reported that their solvent did not contain any of the chemicals on the USEPA List of Lists. According to the MSDS they provided, the solvent does not contain any carcinogens listed by the International Agency for Research on Cancer (IARC), American Conference of Governmental Industrial Hygienists (ACGIH), U.S. Occupational Safety and Health Administration (OSHA) or the U.S. Department of Health and Human Services National Toxicology Program (NTP). The MSDS also states that there are no constituents in the solvent that have any published exposure limits identified by ACGIH as a Threshold Limit Value (TLV) or by OSHA as a Permissible Exposure Limit (PEL), suggesting the solvent does not have any recognized hazardous chemicals. The primary health hazards are derived from the material being corrosive (e.g., eye burns, skin irritant and inhalation irritant).

The objective of the evaluation was to determine if there were any unacceptable environmental, health or safety concerns that may prevent implementation or environmental permitting of similar pilot scale plants and aa larger scale facility. In the event, significant concerns were identified, the assessment was to include possible measures to reduce the concerns and incorporate these measures into future designs and operation.

2.0 SITE DESCRIPTION

2.1 Location

The E.W. Brown Generating Station is located at 815 Dix Dam Road in Harrodsburg, Mercer County, Kentucky. It is located approximately 7 miles north/northeast of Harrodsburg, Kentucky and 9 miles southwest of Nicholasville, Kentucky. Approximate latitude and longitude are: 37° 47' 21" north, 84° 42' 55" west. Approximate elevation is 890 feet above mean sea level. A Site Location Map has been included as **Figure 1** in this report.

2.2 Site Land Use

Site land use is industrial within an existing power generating station. The footprint for the power plant contains greater than 20 acres and includes a hydroelectric plant, three coal-fired generating units, six combustion turbines and associated raw material and fly ash handling operations.

Site land use was not altered or adversely affected by the pilot project. The project footprint was less than 0.25 acre and located entirely within the existing station footprint. Project equipment was installed next to an existing building. Researchers were on site to operate the pilot plant and perform continuous emission monitoring activities. EPRI also had a laboratory to conduct independent sampling at the host site. Existing roads and parking areas were utilized. Traffic followed existing roads within the power plant and no new right of ways were required or disturbed by the project.

2.3 Adjacent Land Use

No local, state or federal parks, forests, monuments, scenic waterways, wilderness or tribal lands are located near the project site. The power plant is located near Herrington Lake, which is used for recreational purposes as well as the water supply for the hydroelectric plant and coal-fired power units. The lake is approximately 1,100 feet south/southeast of the pilot project work area (reference **Figure 2).**

2.4 Cultural, Recreational and Environmentally Sensitive Features

According to the Harrodsburg/Mercer County Tourist Commission, Herrington Lake is a 3,600-acre lake popular for many outdoor recreational activities. The lake was created by construction of a dam across the Dix River. Herrington Lake is about 35 miles long, up to 1,200 ft. wide and has over 325 miles of shoreline. The deepest area is near Dix Dam where water depth reaches 249 feet. The estimated capacity of the lake is 175,000,000,000 gallons (http://www.hlcl.org/joomla15/index.php?option=com_content&view=article&id=47&Itemid=54).

Dix River Dam (Structure ID No. 88003384) is listed on the National Register of Historic Places. It was added to in 1990 for its historic significance in architecture and engineering design.

The pilot project was a relatively small facility located on the grounds of the existing E.W. Brown power plant, isolated from Herrington Lake and Dix River Dam. The pilot project did not have any adverse impact on either of these resources.

3.0 PROCESS DESCRIPTION

3.1 E. W. Brown Generating Station Description and Tie-In

E.W. Brown Generating Station was the host site for the pilot plant and related equipment. The pilot project was located with accessible proximity to the flue gas duct work, electrical and water utilities without impacting resource demand for the host utility. The flue gas slipstream was collected after the WFGD unit. Pilot project effluent was re-injected into the flue gas in adjacent ports after the WFGD unit (refer to **Figure 3**).

3.2 UKy-CAER Unit Description and Process Flow

The project included the installation of a series of process vessels (tanks and columns) and their support equipment to remove impurities and CO_2 from the flue gas. System equipment includes: a shell-tube gas-gas heat exchanger; a direct contact cooler-type pre-treatment tower for polishing flue gas contaminants; a packed column scrubber; two packed-bed strippers with reboiler and reclaimer (strippers); an integrated cooling tower; balance of plant consisting of several heat exchangers for heat recovery; several pumps for liquid recirculation; and a filtration device to remove entrained slurry droplets from the SO_2 scrubber and solids formed during the process. Additionally, several pre-filters were installed prior to the circulation pumps.

The flue gas is treated in the SO_2 pretreatment tower to remove sulfur and reduce other impurities by using a sodium carbonate (soda ash) solution. Following the pretreatment tower, the flue gas enters the CO_2 absorber column. The CO_2 in the flue gas is absorbed into the liquid solvent solution (MEA or H3-1) in this column making the solution rich in CO_2. The gas stream was then re-injected to the power plant flue gas after the WFGD. The air strippers, reclaimer and reboiler are support units to remove CO_2 from the solution and recondition the solvent for return to the absorber.

Process water was needed for non-contact cooling and make up throughout the system. Estimated volumes from the initial EHS Assessment (SMG, 2012) are presented below and were consistent with actual operating conditions. Due to the relatively low water demand (as compared with that required by the power plant), make up water was obtained from the E.W. Brown water supply.

Slipstream process inputs include the following:

Table 1 CCS Raw Material Inputs

Raw Material Input	Planned Rate
MEA	2.1 kg/d
Hitachi H3-1 solvent	≤ 2.1 kg/d
Flue gas stream entering slipstream	1,400 ACFM
Sodium Carbonate solid	50.5 kg/d
Water (non-contact cooling makeup intake)	33,600 kg/d (1400 kg/h)
Water (cooling water process recirculation)	7,680 kg/d (320 kg/h)

kg/h = kilograms per hour

kg/d = kilograms per day

ACFM = actual cubic feet per minute

4.0 EH&S EVALUATION

4.1 Solvent and Degradation Products Toxicity and Risk

4.1.1 Introduction

Prior qualitative and quantitative health risk assessments were prepared for the proposed operation of the PCCCS using amine based solvents (MEA and Hitachi H3-1) in a 0.7 MWe pilot plant at the E.W. Brown Generating Station (SMG, 2012; ENRISQ and SMG, 2013). These preliminary evaluations concluded that MEA, H3-1 their likely degradation products and other materials used at the pilot plant pose little human health or ecological risk when proper safety, handling, and industrial hygiene procedures are followed. The solvents may cause irritation to eyes, skin or the respiratory system if direct contact occurs. If nitrosamines are generated as degradation products of the capture solvents, they may pose significant human health and ecological risks. The potential for generation of nitrosamines, even at relatively low concentrations, was deemed the most significant potential human health risk.

UKy-CAER operated the pilot plant with MEA and performed testing from May 26, 2015 through January 14, 2016 and operated with Hitachi H3-1 performing testing from February 20, 2016 through July 14, 2016. This quantitative evaluation of potential health risks to study workers was conducted using the analytical results from samples collected during testing campaigns in 2015 and 2016.

A literature review identified several reports that discuss potential health risks associated with amines used in CO_2 capture. A report by the Norwegian Institute of Public Health, *Health Effects of Different Amines Relevant for CO_2 Capture* (NILU, February 2009) presented health effects information for MEA, piperazine, aminomethylpropanol (AMP) and methyldiethanolamine (MDEA). The report concluded all these amines appear to cause irritation, but only piperazine was reported to be sensitizing (causing an allergic reaction). There were also indications that amines may be reproductive and developmental toxins. There was no indication these amines were carcinogenic.

An additional report from the Norwegian Institute for Air Research: Summary Report: *Amine Emissions to Air During Carbon Capture, Phase I: CO_2 and Amines Screening Study for Effects* *to the Environment* (NILU: OR 8/2009, March 2009) also studied MEA, AMP, MDEA, and piperazine. The study concluded that the amines themselves likely pose little risk to human health but may contribute to nitrogen loading and may cause eutrophication in sensitive ecosystems. Oxidative degradation products of the amines may be formed that include nitrosamines, nitramines, aldehydes, and amides. The nitrosamines are a concern, since they can be toxic and carcinogenic at extremely low levels of exposure.

A report from the Bellona Foundation dated September 2009: *Amines Used in CO_2 Capture – Health and Environmental Impacts* (Shao, et al, Bellona, 2009), studied the amine solvents used for CO_2 capture. The study distinguished between potential health risks related to the use of MEA compared to potential health risks associated with AMP, MDEA, and piperazine. The report concluded that MEA has a higher biodegradability than the other amines and would not be expected to have a direct adverse effect on human health or ecological receptors. It may, however, cause eutrophication when emitted in high concentrations. The other amines (AMP, MDEA and piperazine) were thought to have a higher ecotoxicity, lower biodegradability and higher environmental impact when compared to MEA. The report also concluded that most of the degradation products of the amines will not have environmental impacts. The nitrosamines, however, are likely to be the degradation products with the most adverse potential risks.

Carbon capture systems (CCS) have not been widely studied for coal-fired boilers, however, degradation of the process solvent was anticipated to occur through irreversible side reactions with carbon dioxide and other flue gas components (Strazisar, Anderson and White, 2003). A study to determine the potential human health and environmental impacts of emissions for several amines, including MEA, from carbon capture and storage operations was conducted by the Norwegian Institute for Air Research. The study concluded that the risk of exposure to MEA was low; however, the study acknowledged that additional research was warranted to evaluate the photo-oxidation of the amines in the atmosphere with nitrogen oxides, which may produce compounds, like nitrosamines, nitramines and amides, which are of higher concern and may pose some risk to human health and the environment (Knudesen, Karl and Randal, 2009).

A product safety assessment published by the Dow Chemical Company (2010) indicates that MEA, a primary amine, does not directly react with nitrites to produce nitrosamine. Similarly, a study published in Science Direct (Fostas, Gangstad, Nenseter, Pedersen, Sjovoll and Sorensen, 2010) evaluated the effects of nitrogen oxides in flue gas upon the degradation of MEA. This investigation concluded that although MEA is less likely than other amines to form nitrosamines, a secondary amine (diethanolamine (DEA)) produced from MEA degradation can be converted to nitrosamines (e.g., N-nitrosoethanolamine (NDELA), non-volatile; N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR), both volatile). The study concluded that further research on the topic was warranted.

More recent studies (Zhang, et al, 2014; SEPA, 2015) have evaluated nitrosamine emissions from CCS facilities and determined there does not appear to be a significant health risk for potential emissions from a pilot plant at the scale operated.

4.1.2 Materials and Methods

The methodology used to conduct this quantitative evaluation is consistent with the Risk Assessment Guidance for Superfund (RAGS) developed by the USEPA. The evaluation focused primarily on potential health risks related to possible exposures to nitrosamines which may result from degradation of the CO_2 capture solvents. The assessment was based on potential exposures during the megawatt-scale PCCCS study at the EWB facility and analytical results obtained during the study.

Analytical results were obtained from several sources. CB&I Environmental & Infrastructure, Inc. performed system exhaust stack testing on two separate occasions. The results for the first testing were provided in a report entitled: *Emission Test Report Stack Test Campaign No. 1, Megawatt-Scale Pilot Carbon Capture System Operated by the University of Kentucky Center for Applied Energy Research (CAER), E.W. Brown Station-Kentucky Utilities, Harrodsburg, Kentucky* (CB&I, March 15, 2016). This report presented results for samples collected between September 29 and October 2, 2015. The results for the second testing were provided in a report entitled: *Emission Test Report Stack Test Campaign No. 2, Megawatt-Scale Pilot Carbon Capture System Operated by the University of Kentucky Center for Applied Energy Research (CAER), E.W. Brown Station-Kentucky Utilities, Harrodsburg, Kentucky* (CB&I, July 27, 2016). The second report presented results for samples collected between June 5 and 7, 2016.

Additionally, nitrosamine results for MEA testing were provided by the UKy-CAER and Hitachi provided nitrosamine data for the H3-1 testing campaign.

The analytical results used in this risk assessment are summarized in **Appendix B, Table 1**. The data are categorized by the capture solvent used during the testing, MEA or Hitachi H3-1, and by the location the sample was collected (i.e., the Primary Absorber Outlet or the Secondary Stripper Outlet) and by entity that collected/analyzed the samples, either CB&I, UKy-CAER, or Hitachi.

To have consistent units of concentrations, sample results were typically converted to $\mu g/m^3$ using formulae presented in **Appendix B, Table 1**. Constituents of Concern (COCs) identified in the samples and evaluated in this assessment were: acetaldehyde, acetophenone, ammonia, formaldehyde, MEA, propionaldehyde and nitrosamine (generic). The range of detected concentrations for each COC, at each sample location, as a function of CO_2 capture solvent is also presented in **Appendix B, Table 1**. Additional compounds detected during testing were arsenic, chromium, isophorone and lead, which are constituents of the coal fired flue gas prior to treatment and were not considered in this assessment.

4.1.3 Toxicity Assessment

A toxicity assessment of the solvents, other raw materials and potential solvent degradation products was completed in the initial EH&S assessment completed in 2012 (SMG, 2012). The primary health concern identified for the unused CO_2 capture solvents is the corrosive nature of the materials. Direct exposure to the solvents may cause severe skin irritation, damage to the eyes, mouth, throat, and respiratory system. Some of the compounds may also cause allergic reactions and a few have been identified as reproductive toxins. If these exposures are prevented through proper process and sampling technique and the use of personal protection equipment (PPE), then the corrosive nature and other toxicities of the solvents were mitigated. The solvents have not been identified as possible human carcinogens. Low level exposures to pure solvents which may be present in ambient air are not expected to result in human health risks.

An additional health concern identified in the initial EH&S assessment was the potential cancer risk from exposure to nitrosamines derived from solvent use and degradation. Materials such as MEA, Hitachi H3-1, piperazine isomers and other secondary and tertiary amines may be nitrosated during the solvent capture process and generate nitrosamines. While direct exposures to the solvents may be prevented, and low-level exposures through ambient air inhalation to pure solvents have not been identified as posing a cancer risk, inhalation exposures to nitrosamines in ambient air or during process sampling may pose a cancer risk to study workers.

Toxicity information and risk-based screening concentrations for inhalation exposures to detected constituents of concern (COCs) were obtained from the USEPA Regional Screening Level (RSL) Summary Table (May 2016, verified November 2016). EPA published RSLs for detected COCs are presented in **Appendix B, Table 2**. EPA has not published RSLs for MEA, Hitachi H3-1 or generic nitrosamines (Hitachi did not provide specific isomer concentrations). To evaluate potential health risks for exposures to MEA, the OSHA PEL and ACGIH TLV were used to determine if detected concentrations exceeded acceptable standards for workplace inhalation exposures.

To evaluate exposure to nitrosamine concentrations, RSLs for specific nitrosamine isomers were considered and used to develop a surrogate value for consideration. The compounds used as surrogates were: N-nitrosodiethanolamine, N-nitrosodiethylamine, N-nitrosodimethylamine and N-nitrosodimethyldiethylamine. The most toxic (strongest carcinogen) of these with the lowest RSL is N-nitrosodiethylamine, with an RSL of 2.9E-04 µg/ m^3. The least toxic (a weaker carcinogen) with the highest RSL is N-nitrosodiethanolamine with an RSL of 1.5E-02 µg/ m^3. An average of the RSLs for these surrogate compounds was used to assess potential health risks. That value is 4.5E-03 µg/ m^3. It should be noted that the RSLs for these surrogates had a range of approximately 2 orders of magnitude. Use of the surrogate average value may over estimate or underestimate potential cancer risks associated with exposures to nitrosamines.

The primary health concern related to nitrosamines is cancer risk, even at relatively low levels of exposure. The industrial (workplace) ambient air screening levels (RSLs) for the individual nitrosamines at a cancer risk level of 1E-6 (one-in-a million) is based on workplace exposures occurring 8 hours per day, 250 days per year for 25 years. This is a total of 50,000 hours of exposure through inhalation, which is substantially greater than likely exposures during the pilot test, but may be considered for full-scale operations.

4.1.4 Exposure Assessment

A complete exposure assessment quantifies the potential level(s) of exposure to specific compounds and their environmental concentration(s). Exposures may occur through inhalation, dermal contact and/or ingestion. Ingestion of compounds in an environmental exposure scenario is usually considered to be unintentional and is classified as incidental ingestion. For purposes of this evaluation, incidental ingestion of materials used at the CO_2 capture pilot study is considered negligible and was not further evaluated. Based on discussions with UKy-CAER members, appropriate personal protection equipment (PPE) such as safety glasses, laboratory coats and chemical-resistant gloves were used during the study. Therefore, dermal exposures are also considered to be negligible. Therefore, inhalation is the primary route of exposure evaluated in this assessment.

For the initial exposure assessment, standardized exposure parameters were used that reflect normal occupational exposures. These exposure parameters are: workplace exposures occurring 8 hours per day, 250 days per year for 25 years (50,000 hours of exposure through inhalation). In addition to USEPA RSLs, OSHA PELs and ACGIH TLVs were also used to evaluate potential health risks from occupational exposures. The OSHA and ACGIH values are based on a 40-hour work week and a healthy adult worker. Actual exposures that may have occurred during the sampling events and pilot study would be much less than the parameters used to calculate the RSLs.

Because the RSLs are based on a total exposure time of 50,000 hours reflecting a full-time occupational exposure, a second exposure assessment was conducted that reflects more realistic exposure parameters encountered during the megawatt-scale PCCCS study. This exposure assessment used the relatively limited opportunities for exposure that would occur during sampling events. The information related to these exposures was provided by UKy-CAER members and is discussed in more detail in the risk characterization section of this assessment.

In addition to the parameters of frequency, length of time and duration of pilot plant operation that define the exposure scenario, the exposure point concentration (EPC) of each detected COC determines the level of worker exposure. A limited number of sampling events provided only a few data points (concentrations) for each COC. The range of detected concentrations of each COC, at each of the sampling locations, as a function of the specific CO_2 capture solvent used during the testing (i.e., MEA or Hitachi H3-1) are presented in **Appendix B, Table 1**.

Because the data sets are limited, the maximum detected concentration for each COC was selected as the exposure point concentration for purposes of this risk assessment. The EPCs were then compared to RSLs, PELs, and TLVs as shown in **Appendix B, Table 2** as part of the risk characterization.

4.1.5 Risk Characterization

Risk characterization integrates the toxicity of a compound with the opportunity or level of exposure to estimate the level of human health or ecological risks related to exposures to the compound. The primary health risk evaluated in this study is potential cancer risk from inhalation of nitrosamines. The risk characterization considered a “worst-case” scenario by using RSLs, PELs and TLVs that reflect a full-time occupational exposure, and comparing these allowable exposure values with the maximum concentration of a particular COC. Potential health risks were also characterized (quantified) for more realistic exposures.

As previously discussed, a workplace ambient air RSL for generic nitrosamines was calculated based on the RSLs of surrogate nitrosamine isomers. This RSL is 4.5E-03 μg/m^3 based on 50,000 hours of occupational exposures and a cancer risk level of one-in-a million (1E-06). Actual exposures to nitrosamines were estimated to be much less, occurring only during sampling events or work on the test system.

Information on process-testing-specific exposure frequency and duration was provided in the CB&I air emission test reports, where sampling occurred on September 29 and 30 and October 1 and 2 in 2015 as well as on June 5, 6 and 7 in 2016 (7 days total). The reports indicate that sampling occurred multiple times through the day lasting 1 to 2 hours per testing event. Hitachi reported generic nitrosamine results for sample dates in May and June 2016 (May 3, 6, 10,11 and June 8). UKy-CAER reported no detected concentrations for all specific nitrosamine compounds analyzed, with limits of quantitation ranging from 0.058 – 9.16 ppbV (0.205 – 1968.4 ug/m^3) for air emissions with no specific sample dates. For purposes of this risk assessment, a full 8-hour work day of exposure was used for each sampling day.

The maximum detected COC concentrations were used as the EPCs and compared to full-time employee risk-based and regulatory occupational acceptable levels (USEPA RSLs, OSHA PELs and ACGIH TLVs, see **Appendix B, Table 2**). Using MEA as the capture solvent, the maximum detected air emission concentration for ammonia at the primary absorber and secondary stripper exceeded the USEPA RSL and occupational exposure thresholds (PEL and TLV). Maximum detected air emission concentrations for MEA exceeded occupational thresholds at the primary absorber and secondary stripper (MEA has no RSL). MEA concentrations at the primary absorber and secondary stripper also exceeded the ACGIH Short-term Exposure Level (STEL, 15,000 μg/m^3). Maximum detected air emission concentrations at the primary absorber for formaldehyde exceeded respective USEPA RSLs. Finally, the maximum detected concentration of formaldehyde at the secondary stripper exceeded the USEPA RSL and occupational exposure thresholds (PEL and TLV).

Constituent concentrations exceeding occupational exposures do not necessarily indicate a cause for employee exposure concern, because employees would not be exposed to air emissions from these sources for 8 hours per day, 5 days per week for 30 years. Similarly, constituent concentrations detected above USPEA RSLs do not necessarily indicate a community concern for ambient air quality due to the emissions being diluted in the exhaust stack for the generating station. However, elevated concentrations of ammonia, MEA and possibly formaldehyde detected at the secondary stripper and extrapolated to a large-scale facility warrants additional evaluation and possibly consideration of additional emission control measures, if this exhaust stream will not be directed to the power plant boiler.

Results for amine emission concentrations were not available for the Hitachi H3-1 campaign. Relative to the MEA campaign, maximum detected concentrations of acetaldehyde were comparable; ammonia was considerably lower; and formaldehyde was higher. Maximum detected concentrations for formaldehyde at the secondary stripper outlet exceeded full-time occupational exposure thresholds and USEPA RSLs. Maximum detected concentrations for acetaldehyde, ammonia (secondary stripper only), formaldehyde (primary absorber only), and propionaldehyde (secondary stripper only) exceeded USEPA RSLs, but not occupational thresholds.

As mentioned earlier, nitrosamines were not detected by UKy-CAER (0.204 – 8.358 *u*g/m^3 LOQ range) during the MEA campaign. Nitrosamines were identified as a generic form by Hitachi during the H3-1 campaign at calculated concentrations ranging from 6.5 – 6,480 *μ*g/Nm^3 at the primary absorber and 42.48 – 47.16 *μ*g/Nm^3 at the secondary stripper. If nitrosamines were created during the MEA campaign at concentrations within the LOQ range, they would exceed the extended exposure time USEPA RSL of 4.5E-03 *μ*g/m^3. Reported values for the "generic nitrosamine" compound for the H3-1 campaign all exceeded the USEPA RSL.

Using an 8-hour exposure duration and 7 days of testing exposure (56 hours total), a more specific risk-based screening level was calculated to reflect more reasonable testing exposures. This is nearly a 1,000-fold decrease in exposure time compared to the full-time occupational scenario: 50,000 hrs. / 56 hrs. = 893. To achieve the equivalent dosing amount of the RSL, through inhalation exposures during sampling events, an 893-fold increase in the ambient air concentration would be required. Therefore, a project specific risk-based screening level for nitrosamines is 893 times the RSL of 4.5E-03 *μ*g/m^3 or 4 *μ*g/m^3, for a cancer risk level of 1E-06. Under this scenario, and if nitrosamines were detected at or below the middle of the LOQ range reported for nitrosodiethylamine during the MEA campaign, the EPC would be below the more specific calculated RSL. However, test results for the H3-1 campaign were still above the more specific calculated RSL.

For risk assessments, the USEPA uses an acceptable cancer risk range of 1E-06 to 1E-04 (one in one million to one in ten thousand) for occupational exposures. A risk-based screening value for nitrosamines at the 1E-04 risk level is approximately 400 μg/m^3. The nitrosamine EPC at the Primary Absorber Outlet during the H3-1 campaign still exceeds this value. The EPC at the Secondary Stripper, however, does not. There are no PELs or TLVs available for nitrosamine. Rather, there is a general standard of care that occupational exposures to carcinogens should be kept as low as possible.

4.1.6 Uncertainty Analysis and Data Needs

Areas of uncertainty with respect to evaluating potential health impacts were identified during the assessment, which should be considered in planning for future scale up activities. These were largely due to relatively low acceptable exposure levels for nitrosamines with respect to the accuracy and precision of nitrosamine analysis methods (i.e., detection levels well above acceptable exposure levels). Additionally, specific nitrosamine isomers were not identified in the analytical results from Hitachi for samples collected during the H3-1 campaign and CB&I did not analyze for nitrosamines during either the MEA or H3-1 campaigns.

The data sets available for the risk assessment were obtained from, and analyzed by, multiple entities (CB&I, UKy-CAER and Hitachi) at different times in different locations and reported with different LOQs and units of measure, making it difficult to compare and evaluate potential impacts uniformly. Also, analytical results varied by multiple orders of magnitude, complicating the evaluation of impacts and comparing impacts for each solvent.

The exposure assessment was based on estimated exposures during sampling events. Actual exposure durations, frequencies and exposure point concentrations likely varied, but it is not believed substantially. Additional specific monitoring of ambient air exposures during plant operation would be helpful to better characterize potential health risks to workers.

A specific risk-based screening value for MEA was not publicly available. An average screening value of several nitrosamines was used rather than a compound specific value because either specific nitrosamine isomers were not identified by Hitachi or all isomers analyzed by UKy-CAER were reported below LOQs.

The uncertainties of the analytical results, specific exposure concentrations, specific exposure parameters and specific toxicity values contribute to uncertainty in the results of the risk characterization. However, the evaluation provides a reasonable consideration of potential impacts that need to be explored further for any potential scale-up. More detailed exposure data with additional sampling and analytical testing is warranted to reduce uncertainties related to exposure concentrations and subsequent risk characterizations.

4.1.7 Risk Characterization Conclusions

Direct exposure to CO_2 capture solvents should be avoided and PPE should be used to avoid possible irritation and other toxicities. Formation of nitrosamines may occur from the degradation of MEA and did occur with the use of H3-1 during the capture process. Assessment of potential exposures to nitrosamines during the study indicates that researcher exposure levels may result in cancer risk exceeding USEPA acceptable risk ranges of 1E-06 to 1E-04. Given this, exposures to process gases should be avoided. Additional assessment of expected actual exposure frequencies, durations and concentrations of specific nitrosamines at lower detection levels is warranted to better characterize potential health risks.

Due to uncertainties in the exposure scenarios considered and data generated, extrapolating these results to operation of a large scale PCCCS may not accurately identify potential risks of nitrosamine exposure by site workers or the surrounding community. However, it is reasonable to presume that a larger scale facility will consume greater amounts of solvent. Depending upon the solvent formulation, a larger scale facility may generate relatively larger amounts of nitrosamines, albeit at similar concentrations due to increased air flow, that could result in greater risk of exposure and harmful health effects without additional emission control measures. Additionally, elevated concentrations of ammonia, MEA and possibly formaldehyde detected at the secondary stripper using MEA or a similar solvent and extrapolated to a large-scale facility warrants additional evaluation and possibly consideration of additional emission control measures, if this exhaust stream will not be diverted to a power plant’s boiler.

4.2 EH&S Impacts for Raw Material Storage

Storage methods and quantities of raw materials were evaluated to identify potential EH&S impacts. Material storage and handling requirements are not significantly different from those that would be required for most other industrial facilities. No unique hazard has been identified for any of the proposed raw materials. The primary raw materials that were used, quantities on site, recommended storage methods and precautions are provided below.

Table 2 Raw Material Storage Recommendations

Raw Material	Description	Maximum Quantity On-Site	Storage Method	Storage Precautions
MEA	Colorless, clear, viscous liquid with ammonia odor	3000 gallons	Store in closed and sealed drums or totes. Do not store in zinc, aluminum, copper, copper alloys or galvanized containers.	Store in cool, dry, well-ventilated area. Avoid contact with strong acids, strong oxidizing agents, iron and halogenated hydrocarbons. Pure MEA is a combustible material – keep away from ignition sources. Dilute solution will not likely be combustible.
Hitachi H3-1	Colorless liquid with amine odor	3000 gallons	Store in tightly closed and sealed, light resistant steel drums.	Store in cool, well-ventilated area away from oxidizing agents and acids. H3-1 is similar to MEA and may be combustible in high concentrations – keep away from ignition sources; dilute solution not likely combustible.
Sodium Carbonate	White powder with a mild odor	1000 pounds	Store in closed container in cool, well-ventilated area.	Avoid excessive heat above 120°F and high humidity. Store away from oxidizers.

Raw Material	Description	Maximum Quantity On-Site	Storage Method	Storage Precautions
Liquid Desiccant (calcium chloride 40%/wt.)	Clear to slightly turbid odorless liquid	1000 gallons	Store in closed non-metal drums or totes. Store in cool, well-ventilated area.	Store away from incompatible materials – concentrated solutions in contact with zinc, galvanized iron or sodium may yield flammable hydrogen gas. Corrosive to some metals.

Hazards and precautions listed are based upon information from available (M)SDSs, which may exaggerate actual conditions for dilute solutions.

Planning and reporting requirements under EPCRA apply for more than 10,000 pounds of any chemicals stored on site, with a lower threshold for listed extremely hazardous substances. This would apply to the two amine solvents. The site is required to submit notification, SDSs and Tier II reports to the Kentucky Emergency Response Commission (KYERC), the Local Emergency Planning Committee (LEPC) and the local fire department. These are common requirements for an industrial facility and do not represent a significant environmental concern.

Additional provisions of EPCRA apply to Extremely Hazardous Substances (EHSs) which are listed in Title 40 of the Code of Federal Regulations, Part 355, Appendices A and B. No EHSs were identified in the raw materials.

4.2.1 Air Emissions

Section 4.2 outlines the types and quantities of raw materials stored on-site and associated air emissions. It was not anticipated that a significant amount of air emissions would be generated from the quantities/types of raw materials stored at the E.W. Brown Generating Station PCCCS during the evaluation period (SMG, 2012). Review of air emissions from raw material storage at the pilot plant and extrapolated for a large-scale facility are presented below.

4.2.1.1 Observed Air Emissions for a 0.7 MWe PCCCS

Emissions generated from the storage of raw materials are attributed to storage vessels that contain organic liquids (e.g., MEA and H3-1 solvent) are generated from evaporative (e.g., through rim seals, tank fittings) and working losses. From review of the volumes of process raw materials stored/consumed during the PCCCS evaluation period (May 2015 – July 2016), the emission estimates provided in the Initial EH&S Assessment (SMG, 2012) for process raw material storage were representative of actual emissions observed during the evaluation period. **Appendix C-1** contains a summary of emissions from the operation of the 0.7 MWe PCCCS, including emissions from storage of process raw materials.

4.2.1.2 Potential Air Emissions for a 550 MWe PCCCS

The quantity of process raw materials stored on site will increase significantly when scaling up from a 0.7 MWe to 550 MWe facility. While the air emissions from process raw material storage are expected to be minimal when compared to the total air emissions from operation of a 550 MWe PCCCS, it is important to evaluate if previous assumptions used for the smaller scale PCCCS remain valid for use in determining potential and/or actual emissions from a larger PCCCS.

As noted in **Section 4.2.1**, the methodology used to determine potential air emissions from process storage vessels was observed to accurately characterize air emissions from the 0.7 MWe PCCCS. Thus, the use of basic emission factor principles outlined in the Environmental Protection Agency's, AP-42, *Fifth Edition, Volume I, Chapter 7: Liquid Storage Tanks*, and its referenced software (EPA TANKS Version 4.0.9d), is suitable for use in determining air emissions (potential or actual) from raw material storage vessels for a 550 MWe PCCCS. This emission estimation methodology assumes the use of good housekeeping procedures for storage and transportation of raw materials. Without the use of such measures, evaporate and working losses from raw material storage vessels will increase.

Determination of potential emissions was performed (using extrapolated values) to assess potential environmental risks from raw material storage at an increased scale. **Appendix C-2** contains a summary of potential emissions for the operation of a 550 MWe PCCCS, including emissions from storage of process raw materials. Further evaluation of emissions generated from the bulk delivery and transportation of process solvents is warranted when primary and secondary delivery methods (i.e. – rail car or tanker truck deliveries) are known. It is recommended that vapor recovery systems be considered when delivering truck or railcar quantities of raw materials to minimize air emissions from large-scale PCCCS operations.

4.2.2 Water/Wastewater Management

Non-contact cooling water was required for the cooling tower. The water was pumped through various heat exchangers within the system. Make up water was required for the CO_2 absorber and pretreatment tower. All water used was obtained from the E.W. Brown Generating Station's existing permitted water intake. Therefore, no permitting for water use was required.

The project construction area was located on existing, disturbed industrial property and was approximately 0.25 acres in size. Stormwater permits for new disturbances from construction activities are required by the Kentucky Division of Water for disturbances of 1.0 or more acre in size. Due to its small footprint and location at an active industrial facility, the pilot project did not require a construction permit for storm water discharges.

4.2.3 Waste Management

According to the USEPA Facility Registry System (web site accessed February 8, 2017), the E.W. Brown power plant is registered as an active, conditionally exempt small quantity generator (< 100 kg/month) of hazardous waste. A waste determination was required for each solid waste generated as part of the project. All solid wastes were disposed off site in strict accordance with RCRA requirements. Wastes volumes from spills or materials remaining at the end of the project were minimized by using a well-managed material handling system to avoid spills and minimize excessive inventory requiring disposal at the end of the project.

4.2.4 Employee Hazards

The raw materials have constituents identified as hazardous chemicals and are required by OSHA to be appropriately managed to avoid employee injury. Primary hazards for chemicals are summarized below for each raw material. Hazards and precautions listed are based upon information from available (M)SDSs, which may exaggerate actual conditions for dilute solutions.

Table 3 Raw Material Health Hazards

Raw Material	HMIS Rating	Hazards	Precautions	Exposure Controls
MEA	3	Irritant, hazardous for eye contact or ingestion. Hazardous in case of skin contact and inhalation. Combustible in concentrated form. Corrosive. May be toxic to kidneys, lungs or liver.	Avoid contact with skin and eyes and inhalation. Avoid heat and ignition sources. Provide adequate ventilation.	Use face shield, chemical protective clothing, appropriate respiratory protection, boots and impermeable gloves.
Hitachi H3-1	3	Harmful if swallowed. May be toxic in contact with skin. Causes skin burns and eye damage	Avoid contact with skin and eyes. Avoid inhalation of mist, vapor or spray. Provide adequate ventilation.	Use appropriate respiratory protection, chemical protective clothing or apron, safety boots, and impermeable gloves.
Sodium Carbonate	1	Irritant with skin contact, inhalation and ingestion	Avoid unnecessary exposure and wash after contact	Use impermeable gloves and safety glasses.
Liquid Desiccant (calcium chloride 40%/wt.)	0	Prolonged contact with skin may cause irritation or burns. Avoid contact with skin, eyes or clothing. Avoid breathing mist.	Avoid contact with skin and eyes. Avoid inhalation of mist, vapor or spray	For misty condition, use appropriate respiratory protection. Do not use contact lenses.

The primary, acute hazards are from handling MEA and H3-1, each of which is identified as being corrosive and irritants to skin, eyes and the respiratory system. Personnel handling these materials and all other raw materials were informed of the potential hazards and appropriate protective measures, and appropriately trained consistent with the OSHA Hazard Communication Standard. The identified hazards and recommended protective measures are consistent with good industrial hygiene practices and do not suggest that these materials represent an unusual concern for an industrial facility.

4.2.5 Community Impacts

The project occupied a small portion of the E.W. Brown Generating Station (refer to **Figure 3**). Raw material receipt and consumption were minor relative to quantities used by the power plant as was construction and operating employee traffic. There were no significant community impacts.

4.3 EH&S Impacts for Chemicals Used in Process

4.3.1 Air Emissions

A slipstream from the E.W. Brown Generating Station's flue gas was fed into the pilot PCCCS (see **Figure 4** for a process flow diagram) for two process solvent evaluation campaigns (MEA and H3-1) between May 2015 and July 2016. During this period, UKy-CAER personnel evaluated CO_2 capture efficiencies for both process solvents to determine their viability for use in a larger scale PCCCS. In addition to monitoring parameters of process operations, emissions testing was conducted by UKy-CAER and CB&I Environmental & Infrastructure, Inc (CB&I). UKy-CAER conducted air emissions testing for each solvent and solvent degradation products at the primary absorber and the secondary stripper from May 26, 2015 through January 14, 2016 for the MEA campaign and May 20, 2016 through July 14, 2016 for the H3-1 campaign. CB&I conducted stack sampling and analytical support from September 29 through October 2, 2015 during the MEA campaign and June 5 through June 7, 2016 during the H3-1 campaign. Test data reported by UKy-CAER and CBI was used to determine actual air emissions from operation of the 0.7 MWe PCCCS and potential air emissions for a 550 MWe PCCCS.

An initial analysis (SMG, 2012) of data provided by UKy-CAER estimated that maximum annual potential emissions (operating 24 hours and 365 days) from the 0.7 MWe PCCCS would be relatively low (< 0.4 E-03 tons/year, excluding CO_2). Testing results during operation demonstrated that air emissions for criteria pollutants were higher (about 2.85 tons of actual emissions with a calculated maximum annual potential of about 6.53 tons). Although actual air emissions were higher than estimated, operation of this pilot plant for limited hours as a research and development facility should still qualify as an Insignificant Activity (IA); however, if the pilot plant were operated more than 6700 hours per year, the E.W. Brown facility may be required to modify its Title V air permit. More detailed discussion of actual and project air emissions is presented below.

Actual air emissions derived from test results completed by UKy-CAER and CBI during operation of the 0.7 MWe PCCCS are discussed in **Section 4.3.1.1** below. To augment these emission calculations, **Section 4.3.1.2** reviews potential emissions derived from the results of testing MEA solutions in the system for degradation products (expected vs detected). **Section 4.3.1.3** contains a Potential-to-Emit (PTE) analysis for a 550 MWe PCCCS using extrapolated values for system operating parameters (i.e., gas flow rates) and pollutant emission rates (based on emissions testing results from UKy-CAER and CB&I).

4.3.1.1 Measured Air Emissions

Volumetric/gravimetric pollutant concentration data from emissions testing (CB&I, March 2016 and UKy-CAER), measured gas flow rates for the 0.7 MWe pilot PCCCS, and AP-42 emission factors were combined to determine air emissions during the evaluation period of May 2015 through July 2016 (see **Appendix C-1** for detailed calculations). **Table 4** below summarizes the calculated air emissions from the MEA campaign.

Table 4 PCCCS (0.7 MWe) Air Emissions Summary

Regulated Air Pollutant	Actual Emissions(a) (tons)	Maximum Potential Emissions(f) (tons/year)
Single HAP	0.020	0.064
Combined HAPs	0.026	0.085
CO (b)	N/A	N/A
NO_X (b)	N/A	N/A
Lead (Pb) (b)	N/A	N/A
VOCs	1.999	6.51
SO_2 (c)	-0.017	-0.06
PM_{10}	0.025	0.083
Ammonia [112(r) RAP] (d)	1.173	3.82

Notes:

(a) Total emissions based upon the sum of the operating hours for the MEA Campaign (1,316 hours) and the H3-1 Campaign (1,375 hours), ~ 2,691 total hours.

(b) There are no emissions of CO, Lead, or NOx from normal operation of the CCS system, these pollutants are in the flue gas.

(c) SO_2 emissions are negative because the CCS System pretreatment tower removes SO_2 from the flue gas slipstream.

(d) Anhydrous ammonia is a regulated air pollutant under the CAA 112(r) Risk Management Program, but there is no applicable requirement for non-anhydrous ammonia from the PCCCS because any anhydrous ammonia present would be less than the threshold quantity in 40 CFR §68.130, Table 1.

Additionally, anhydrous ammonia present in a mixture (pilot gas process streams) below 1% by weight need not be considered when determining whether anhydrous ammonia is present above a regulatory reporting threshold (40 CFR 68.115(b)(1)).

(e) CO_2 (GHG) emissions are not included in the PTE summary because the pilot plant temporarily removes CO_2 from the flue gas stream and will return the captured CO_2 to the atmosphere. The CCS system does generate CO_2 emissions from normal process operations.

(f) Maximum annual potential emissions extrapolated to 24 hours/day x 365 days (8,760 hours).

MEA and associated degradation compounds (i.e., - aldehydes, ketones and ammonia) were the largest contributors to actual air emissions during the MEA campaign. As noted in **Appendix B, Table 1**, formaldehyde air emissions from the H3-1 campaign were higher (relative to the MEA campaign) at the secondary stripper and ammonia emissions were substantially lower at both the primary absorber and secondary stripper.

Although actual air emissions were higher than estimated, the relatively small amount of emissions is not anticipated to have adversely impacted surrounding terrestrial or water resources, since they would have been readily diluted and dispersed from the main exhaust stack at the E.W. Brown Generating Station.

4.3.1.2 Solvent Degradation Product Estimates

MEA solutions were tested by UKy-CAER throughout the system to identify degradation compounds and concentrations (due to its proprietary nature, similar testing was not completed on the H3-1 solvent). Twenty-one (21) potential degradation compounds were analyzed (excluding metals) and only eight (8) compounds were detected above the method detection limit (MDL). The following list identifies the compounds analyzed, results and the MDL (if parameter was not detected during sampling).

Compound	Sample Result (ppm)	MDL (ppm)
HEI	4920	
OZD	<MDL	2.4
HEF	<MDL	0.07
HEA	<MDL	16.0
BHEOOX	<MDL	0.07
HEEDA	215.6	
HEIA	1479.0	
Acetaldehyde	0.024-0.0319	
Acetic acid (as acetate)	689	
Ammonia	300	
Formaldehyde	0.035	
Formic acid (as formate)	5,477	
N-nitrosodimethylamine	< MDL	0.022-0.055
N-nitrosodiethanolamine	< MDL	0.022-0.055
N-nitrosodiethylamine	< MDL	0.022-0.055
N-nitrosodibutylamine	< MDL	0.022-0.055
N-nitrosodipropylamine	< MDL	0.022-0.055
N-Nitrosomorpholine	< MDL	0.011 – 0.0275
N-nitrosopiperadine	< MDL	0.022-0.055
N-nitrosopyrrolidine	< MDL	0.022-0.055
Phosphoric acid	< MDL	0.1

For detected degradation compounds that were not analyzed in air emission testing (see **Section 4.3.1.1**), SMG estimated potential air emissions using Henry's law and liquid phase concentrations to calculate a corresponding gas phase concentration for the pollutant. The resultant gas phase concentration for each pollutant was multiplied by measured (**Appendix C-1**) or extrapolated (**Appendix C-2**) process gas flow rates to estimate maximum hourly pollutant emission rates from a 0.7 MWe PCCCS (**Appendix C-1**) or a 550 MWe PCCCS (**Appendix C-2**).

4.3.1.3 Source Classification (0.7 MWe) PCCCS

The installation and operation of the pilot plant at the E.W. Brown Generating Station does not meet the definition of "Modification" as defined under 42 U.S.C. §7470 to §7492, 42 U.S.C. §7501 - §7515, or 401 KAR 52:001, Section 1(51) because: 1) the potential emissions from the project are below the PSD Significant Emission Rates (SER) for CAPs; and 2) none of the equipment associated with the PCCCS is subject to a New Source Performance Standard (NSPS). Categorically, research and development (R&D) activities (0.7 MWe Pilot Scale PCCCS) have exemptions from the Acid Rain and Title V programs. Because the emissions from the PCCCS are below insignificant activity CAP emission thresholds, the IAs submitted[1] for addition to the E.W. Brown Generating Station Title V permit do not violate or affect any existing terms or conditions of the permit. Therefore, installation and operation of the pilot PCCCS processed as an "off-permit" change pursuant to 401 KAR 52:020, Section 17(1) remains valid despite measured increases in actual emissions for the 0.7 MWe PCCCS. Based upon the foregoing, actual air emissions from the operation of the 0.7 MWe PCCCS did not present an unacceptable or insurmountable environmental risk.

4.3.1.4 Potential Air Emissions from a 550 MWe PCCCS

Volumetric/gravimetric pollutant concentration data from the pilot plant testing, extrapolated gas flow rates for the proposed 550 MWe PCCCS and AP-42 emission factors were combined to determine the 550 MWe PCCCS's potential-to-emit (PTE) for CAPs, HAPs and RAPs. PTE calculations assume that the PCCCS will operate 8,760 hours per year at a "worst case" emission rate (see **Appendix C-2** for detailed calculations). **Table 5** below provides a summary of the calculated potential emissions from a large-scale PCCCS.

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[1] Kentucky Utilities Company – E.W. Brown Generating Station submitted a letter "*Re: Kentucky Utilities/E.W. Brown Generating Station (AI #3148) Construction of Slipstream-scale CO_2 Capture System"* on March 25, 2014 to US EPA Region 4 and the Kentucky Division for Air Quality notifying the Administrators of proposed changes at the facility to install insignificant activities (0.7 MWe PCCCS) qualifying for processing as an off-permit change.

Table 5 PCCCS (550 MWe) Potential-to-Emit Summary

Regulated Air Pollutant	PTE [(a)] (tons/yr.)
Single HAP	16.3
Combined HAPs	21.8
CO (b)	N/A
NO_X (b)	N/A
Lead (Pb) (b)	N/A
VOCs	3,888
SO_2 (c)	-38.5
PM_{10}	7.5
Ammonia [112(r) RAP] (d)	1,268

Notes:

(a) 550 MWe PCCCS Potential-to-Emit (PTE) calculations based upon operating 24 hours per day 365 days per year (8,760 hours/year).

(b) There are no emissions of CO, Lead, or NOx from operation of the CCS system; these are in the flue gas.

(c) SO_2 emissions are negative because the CCS System pretreatment tower removes SO_2 from the flue gas slipstream.

(d) Ammonia (anhydrous) is a regulated air pollutant under the CAA 112(r) Risk Management Program mandated for listing by Congress. Because the quantity of anhydrous ammonia present is above the threshold quantity listed in Table 1 to 40 CFR §68.130, the stationary source would be required to develop/revise a risk management plan according the regulations in 40 CFR Part 68.

(e) CO_2 (GHG) emissions are not included in the PTE summary because the removal efficiency for CO_2 from the flue gas stream for a 550 MWe PCCCS is not known. This evaluation was performed to determine air emissions from process operations of a 550 MWe PCCCS and the proper source category (i.e., - PSD Major Source) of the stationary source.

Potential emissions for solvent degradation products listed in **Section 4.3.1.1** from operations of a 550 MWe PCCCS exceed 1,500 tons per year. The highest potential emitting degradation product was ammonia (1,268 tons/yr.). Further evaluation of this scale PCCCS is recommended to make a realistic determination of the potential human health and environmental impacts from air emissions. While the extrapolation methods used in this assessment are useful to estimate order-of-magnitude impacts; specific process data for gas flow rates, solvent liquid flow rates, stack parameters (height, diameter, gas velocity) and flue gas composition are needed to accurately quantify risks/impacts to human health or the environment.

4.3.1.5 Source Classification (550 MWe) PCCCS

Installation and operation of a 550 MWe PCCCS at an existing fossil fuel-fired steam electric plant with a heat input exceeding 250 million BTUs per hour (typical source for PCCCS location) would meet the definition of a “Modification” as defined under 42 U.S.C. §7470 to §7492, 42 U.S.C. §7501 - §7515, or 401 KAR 52:001, Section 1(51) because the potential emissions from the project exceed the prevention of significant deterioration (PSD) VOC Significant Emission Rate (SER) of 40 tons per year. Additionally, a PCCCS at this scale does not meet the R&D exemption provisions in the Acid Rain or Title V permitting programs. Therefore, installation and operation of a 550 MWe PCCCS would be subject to the Major New Source Review (NSR) program applicable to a *Major Modification* at an *existing named source*[2]. While the PCCCS will reduce SO_2 and CO_2, the NSR program is pollutant specific and has no consideration for net emission reductions (e.g. – CO_2 + SO_2 reductions > VOC increases) when considering pollutant control requirements.

Installation of a PCCCS of this scale (*Major Modification*) would, at a minimum, trigger a PSD review that would likely require the source to install best available control technology (BACT) for PCCCS VOC emissions. When a source is required to install BACT, it must determine the maximum degree of control that can be achieved considering energy, environmental and economic impact. If the installation occurred at a source located in a National Ambient Air Quality Standards (NAAQS) Nonattainment Area (i.e., VOCs), the project would also be subject to the Nonattainment New Source Review (NA-NSR) program.

The NA-NSR program requires a source to apply the lowest achievable emission rate (LAER) technology and provide offsets. LAER does not consider economic, energy, environmental or other factors when determining the emission rate achievable for a source. Offsets are an actual emission reduction (from other nearby sources or emission banking programs), supplied in an amount that is greater than or equal to the project’s emission increase. The amount of off sets required (1:1 – 1.3:1) depends on the Nonattainment classification in the area where the project will be located.

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2. *Named sources* are stationary source categories listed in 40 CFR §51.166(b)(1) with a PTE of $\geq$ 100 tons per year (including fugitive emissions) for a regulated pollutant subject to EPA’s New Source Review program for construction of any new major stationary source or any project at an existing major stationary source in an area of attainment or unclassifiable under CAA sections 107(d)(1)(A(ii) or (iii).

In addition to the BACT or LAER requirements of the NSR program, the source would be required to: 1) perform an *Air Quality analysis*; and 2) perform an *Additional Impacts analysis* for the project. The *Air Quality analysis* must demonstrate that new emissions from a *major modification* at an *existing source* will not cause or contribute to a violation of any applicable NAAQS or PSD increment (maximum limit on air quality degradation in an attainment area). The *Additional Impacts analysis* assesses the impacts of air, ground and water pollution on soils, vegetation, and visibility caused by any increase in emissions of any regulated pollutant from the *major modification* and from associated growth (industrial, commercial, and residential growth that will occur in the area due to the source).

A *Major Modification* at an *existing named source* subject to the Major NSR program adds significant requirements to the air permitting process. BACT or LAER control measures for VOC emissions can add significant costs to the installation and operation of a 550 MWe PCCCS. The length of the permitting process for a project subject to the NSR program will often take at least 1.5 – 2.5 years for approval.

4.3.2 Wastewater Management

Process wastewater volumes were approximately 700 gallons per day from the pretreatment tower used to remove sulfur oxides from flue gas prior to CO_2 capture. The pretreatment solution was about 1 - 2% sodium carbonate in water. Wastewater constituents include sodium bicarbonate and sodium sulfates. It was a basic solution (pH 4.6).

An additional wastewater stream was non-contact cooling water from the cooling tower. Blowdown from the tower ranged from about 30 gpm to 90 gpm, yielding approximately 60,000 to 80,000 gallons per day. This water was treated with a descaler, corrosion inhibitor and biocide (sodium hypochlorite) at minor concentrations.

These wastewaters were pumped to the power plant WFGD as a water supplement. No collection, treatment or disposal was required.

Due to the wastewater volumes, contaminant concentrations and ultimate disposal method, wastewater management was not a significant environmental concern while operating the pilot plant. Increased wastewater volumes and constituent concentrations for a larger scale facility will need further evaluation to determine appropriate disposal methods. Recent changes in steam electric power generating effluent guidelines published by the EPA (40 CFR Part 423, published November 3, 2015) will need to be considered to determine any required treatment requirements for surface discharges.

4.3.3 Waste Management

A waste determination is required for each solid waste generated as part of the project. All solid wastes were disposed off site in strict accordance with RCRA requirements. Based upon the preliminary design and information obtained from UKy-CAER, the facility was anticipated to generate the following process solid wastes. Actual wastes reported by UKy-CAER that were generated and disposed off site are also provided in **Table 6** below.

Table 6 Estimated Solid Waste Characteristics and Generation

Waste Stream Description	Generating Process	Primary Characteristics	Estimated Volumes	Actual Volumes
Pretreatment Tower Solids (precipitant from chilled sodium carbonate solution)	System operation of pretreatment tower chiller	Likely non-hazardous solid waste	1.5 kg/hr. 29,329 lbs./year	No solids collected and disposed. Blowdown to WFGD.
Primary Stripper/Reclaimer Waste	System operation of reclaimer	Non-hazardous solid waste with potential to be hazardous for heavy metals if concentrated.	1.6 kg/hr. 31,051 lbs./year	888 gallons, disposed as not hazardous waste.
Spent CO_2 Absorption Solvent Solution (MEA)	Carbon absorber/ stripper operation	Possibly corrosive	Approximately 3,000 gallons per batch	1214 gallons, not a hazardous waste
Spent CO_2 Absorption Solvent Solution (H3-1)	Carbon absorber/ stripper operation	Possibly corrosive	Approximately 3,000 gallons per batch	1265 gallons, hazardous waste due to selenium content
Spent desiccant	Cooling tower operation/ water evaporator maintenance	Possibly toxic (metals) and corrosive	Approximately 8,000 gallons per batch	138 gallons, not hazardous waste
Spent packing materials from: pretreatment tower, CO_2 absorber, solvent recovery column, primary stripper, secondary stripper and cooling tower.	Reactor/Stripping processes and vessel maintenance	Possibly non-hazardous solid waste	Approximately 16,000 gallons per cleaning cycle	Packing materials remain in place, no disposal

Waste Stream Description	Generating Process	Primary Characteristics	Estimated Volumes	Actual Volumes
Foundation wastewater	Water accumulated below system with minor amounts of spilled amine solutions and soda ash	Basic, but not a hazardous waste	Not considered originally	1,684 gallons, not hazardous waste
Heat exchanger wash	Wash out exchanger with dilute acetic acid and water	Acidic	Not considered originally	640 gallons disposed off site as not hazardous waste
Tower/Columns wash water	Vessel cleaning	Possible corrosive or toxic	Approximately 1,500 gallons per cleaning cycle	Approximately 6,500 gallons, not hazardous waste
Spent filters	Pre-pump filtration	Possibly non-hazardous solid waste	Assumed to be a low quantity maintenance item	None discarded
Spent activated carbon from cartridge filter	Filter for slipstream	Possibly toxic (metals)	Not considered originally	440 pounds, not hazardous waste
Chiller coolant	Spent ethylene glycol (50% solution)	Possibly toxic (metals	Not considered originally	275 gallons remain in system, not disposed
Waste oil	Reboiler/Reclaimer operation/ maintenance	Combustible liquid	Approximately 50 gallons per cleaning cycle	< 5 gallons, included below
Waste lubricants and maintenance fluids	Fan, pump and other maintenance	Combustible liquid	Few hundred gallons per year	< 20 gallons, not hazardous waste

Actual waste characteristics were generally consistent with preliminary assumptions. Volumes for some wastes varied (typically smaller quantities) and a few new waste streams (e.g., foundation wastewater, heat exchanger wash and spent activated carbon) were generated. As expected, most wastes were not characterized as a hazardous waste and were approved for disposal off site. No RCRA F, K, P, or U listed wastes were generated and no ignitable, corrosive or reactive hazardous wastes were generated. The one anomaly, was the spent H3-1 solvent, which was characterized as a toxic hazardous waste due to the presence of selenium above the regulatory threshold of 1.0 mg/l.

The types of wastes generated are not unusual for a large industrial facility, and do not represent a uniquely hazardous concern when managed properly. Solid and hazardous were characterized and disposed off-site at permitted waste disposal facilities.

The amount of waste generated by a larger scale facility will increase with the size of the facility, but likely economies of scale should enable the increase to be less than directly proportional to the size increase. Unless further testing of H3-1 is contemplated, site registration and management practices should not be substantially affected to be an unreasonable impact on operations, though waste disposal costs may increase.

4.3.4 Employee Hazards

The E.W. Brown Generating Station is a power plant and likely presents a range of physical hazards to employees typical of industrial facilities. The site has a facility specific worker health and safety program. Employees working on the pilot project were required to adhere to the Station's worker safety programs, as well as any developed worker safety program specific to the proposed slipstream facility project.

Fire hazards exist due to the combustible nature of some of the chemicals used and due to the project equipment. The MSDS for the H3-1 solvent recommends that containers and receiving equipment be grounded. Appropriate protective equipment and measures were employed to prevent injury from exposure to MEA or H3-1. Concentrated calcium chloride solution was isolated from zinc and galvanized iron, since it can react and may yield hydrogen gas which may explode. However, dilute solutions are unlikely to represent a reactivity or fire hazard.

4.3.4.1 Noise

Noise was generated by process pumps and blowers. Internittent exposure to noise by site researchers was mitigated with appropriate hearing protection. Due to the size of the operation (relative to the E.W. Brown facility), noise generated at the pilot plant is not expected to represent a significant concern on the property or to the surrounding community.

4.3.4.2 Hazardous Materials Exposure

(M)SDSs indicate that MEA and the H3-1 solvent could cause acute or chronic health effects to employees. Improper material handling could potentially result in serious inhalation, dermal or ingestion hazards. Storage hazards indicated in the MSDSs were summarized in **Section 4.2.4**. These hazards apply to handling and process area work as well. Eyewash and safety showers were installed near storage and process areas.

4.3.5 Community Impacts

Due to its size, types of activities, limited use of chemicals and location within the E.W. Brown plant site, no significant adverse community impacts were identified from operation of the proposed pilot plant.

4.4 Impact Mitigation Strategies

Potential employee exposures to hazardous chemicals were minimized with appropriate work practices and employee protective equipment. Concentrated forms of the solvents were identified as category 3 health hazards with serious acute hazards. MEA in concentrated form has been associated with long term chronic hazards. Dilute concentrations used on site represented a lower hazard potential. Appropriate personal protective equipment was identified and required to be used to mitigate potential risks to employees.

4.5 Precautions and Accidental Release Measures

General precautions included those typical in industrial work places. Safe handling and storage precautions for the raw materials are discussed in **Section 4.2.4**. Process specific employee hazards were also presented in **Section 4.3.4**. Incompatibilities with materials are summarized in **Section 4.2.4** and more detail is provided in the (M)SDSs in **Appendix A**.

4.5.1 Accidental Release Measures

Specific procedures were developed to respond to an accidental release of hazardous materials. During operation of the pilot plant, there were a few minor spills of process materials, but no significant release of a hazardous material that required implementation of these procedures. Common emergency spill response provisions that were available for the types of chemicals used for this project.

- Avoid contact with skin, eyes and clothing
- Do not breathe vapors or spray mist
- Notify a supervisor immediately
- Evacuate personnel to safe areas
- Keep people away from and upwind of spill/leak

- Stop leak if without risk
- Ventilate the area using a fan that will not cause ignition of the material
- Spill response team should wear appropriate personal protective equipment prior to handling spilled material. Consult the MSDS for the substance for full details.
- After the response is complete, dispose of materials in accordance with applicable regulations.

Facility specific emergency action procedures for ammonia release were also reviewed and available, but not implemented since there were no releases requiring their implementation.

Methods for Clean-up

MEA

Keep away from heat. For small amounts, neutralize, absorb with an inert dry material and place in an appropriate waste disposal container. For large amounts, contain spilled material when possible and pump into suitable and properly labeled containers. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

H3-1 Solvent

Prevent product from entering drains. Take precautionary measures against static discharges. Absorb spill with inert material (e.g. dry sand or earth), then place in a chemical waste container. Large spills should be collected mechanically (remove by pumping) for disposal.

Sodium Carbonate

Sweep up and containerize for reclamation or disposal. Vacuuming or wet sweeping may be used to avoid dust dispersal.

Calcium Chloride

Dilute small spills cautiously with plenty of water. Mop and place into a plastic drum and cover (note that many metals will slowly corrode from this material). Cautiously wash off residue with plenty of water. For large spills, dike up with any available absorbent (commercial, sand, etc.) and transfer into a plastic container and cover.

4.5.2 First Aid Measures

Information provided for first aid measures was taken from (M)SDSs and review of chemical properties of materials used on site.

MEA

Eye Contact:

Wash immediately and continuously with flowing water for at least 30 minutes. Remove contact lenses after the first 5 minutes and continue washing. Obtain prompt medical consultation, preferably from an ophthalmologist.

Skin Contact:

Immediately flush skin with plenty of flowing water for at least 30 minutes, while removing contaminated clothing. Prompt medical consultation is essential. Wash clothing before reuse. Properly dispose of leather items such as shoes, belts, and watchbands.

Inhalation:

Move person to fresh air. If breathing problems or other adverse effects are noted, seek medical attention.

Ingestion:

Do not induce vomiting. Give one cup (8 ounces or 240 ml) of water or milk and transport to a medical facility. Do not give anything by mouth to an unconscious person.

H3-1 Solvent

Eye Contact

Immediately flush with plenty of water. After initial flushing, remove any contact lenses and continue flushing for at least 30 minutes. Immediate medical attention is required.

Skin Contact

Wash off immediately with soap and plenty of water. Obtain medical attention.

Inhalation

Move to fresh air. If breathing is difficult, give oxygen. If not breathing, give artificial respiration. Obtain medical attention.

Ingestion

Never give anything by mouth to an unconscious person. If victim is conscious drink 1 or 2 glasses of water. Do not induce vomiting. Seek immediate medical attention/advice.

Sodium Carbonate

Eye Contact:

Flush eyes immediately with large amounts of water or normal saline solution, occasionally lifting upper and lower lids until no evidence of chemical remains (at least 15-20 minutes). Get medical attention immediately.

Skin Contact:

Remove contaminated clothing and shoes immediately. Wash affected area with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). Get medical attention immediately.

Inhalation:

Remove from exposure area to fresh air immediately. If breathing has stopped, perform artificial resuscitation. Keep person warm and at rest. Treat symptomatically and supportively. Seek medical attention immediately. Qualified medical personnel should consider administering oxygen.

Ingestion:

Give large amounts of fresh water or milk immediately. Do not give anything by mouth if person is unconscious or otherwise unable to swallow. If vomiting occurs, keep head below hips to prevent aspiration. Treat symptomatically and supportively. Seek medical attention immediately.

Calcium Chloride

Eye Contact:

Flush promptly with plenty of water, continuing for at least 15 minutes. Get medical attention.

Skin Contact:

Wash with plenty of water.

Inhalation:

Remove to fresh air.

Ingestion:

If conscious, immediately give 2 to 4 glasses of water, and induce vomiting by touching finger to back of throat. Get medical attention for irritation, ingestion, or discomfort from inhalation.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The scope of this assessment was limited to evaluation of proposed plans and information available from the UKy-CAER and Hitachi as well as a literature review. Process design and operation information was obtained from research conducted by the UKy-CAER. This information included: process flow diagrams; operating parameters; estimated raw material storage and consumption rates; and estimations for air emissions, sample of flue gas, wastes generated and wastewater discharges.

The Hitachi solvent is proprietary and its specific formulation was not available. Hitachi provided MSDS and other general information on their solvent which was relied upon for this initial assessment. From this information, it was presumed that the environmental and health hazards of the Hitachi solvent would not be significantly different than those of MEA.

The objective of the evaluation was to determine if there were any unacceptable environmental, health or safety concerns that may prevent implementation or environmental permitting of the pilot scale plant. If significant concerns were identified, the assessment was to include possible measures to reduce the concerns and incorporate these measures into the actual design and operation of the facility. The results of the assessment serve as a foundation for conducting additional investigation during future plant design and operation to quantitatively evaluate and confirm the extent of potential EH&S impacts for a large-scale (500 MWe) operation and consider potential mitigation measures.

5.1 Toxicity Health Risk Summary

The toxicity associated with MEA and H3-1 is chemical irritation following direct contact. They are not classified as carcinogens and show little, if any, ecotoxicity. Due to possible irritation and other hazards, direct exposure to CO_2 capture solvents should be avoided and appropriate PPE used when handling these materials.

Formation of nitrosamines may occur from the degradation of MEA and did occur with the use of H3-1 during the capture process. Assessment of potential researcher exposures to nitrosamines indicates that exposure levels may exceed USEPA acceptable risk ranges of 1E-06 to 1E-04 for cancer risk. Exposures to process gases should be avoided and process design should consider additional emission control, especially when applied to larger scale pilot facilities. However, uncertainties related to the analytical results, specific exposure concentrations, specific exposure parameters and specific nitrosamine isomer toxicity values contribute to uncertainties of the risk characterization. Additional assessment of expected actual exposure frequencies, durations and concentrations of specific nitrosamines at lower detection levels is warranted to better characterize potential health hazards at pilot scale or larger.

5.2 Air Emissions

This EH&S assessment evaluated environmental impacts of actual air emissions from an operational 0.7 MWe PCCCS located at the E.W. Brown Generating station and potential air emissions from a larger scale (550 MWe PCCCS), presumed to be located at an existing, coal-fired power plant with a heat input exceeding 250 million BTUs per hour. **Section 5.2.1** provides recommendations and conclusions for actual air emissions from the operation of PCCCS located at the E.W. Brown Generating Station. **Section 5.2.2** provides recommendations and conclusions for potential air emissions (extrapolated from data gathered at the E.W. Brown 0.7 MWe PCCCS) for a 550 MWe PCCCS.

5.2.1 0.7 MWe PCCCS Actual Emissions

Initial estimates of maximum annual air emissions for the pilot plant (SMG, 2012) were calculated to be relatively low (< 0.4 E-03 tons/year, excluding CO_2). Testing results during operation determined air emissions were considerably higher (about 2.85 tons actual with a calculated maximum annual potential of about 6.53 tons). Although actual air emissions were higher than estimated, operation of this pilot plant for limited hours as a research and development facility should still qualify as an Insignificant Activity (IA); however, if the pilot plant were operated more than 6,700 hours per year, the E.W. Brown facility may be required to modify its Title V air permit.

MEA with associated degradation compounds (e.g., aldehydes, ketones and ammonia) were the largest contributors to actual air emissions during the MEA campaign. The highest emitting degradation compound was ammonia (1.66 tons). For the H3-1 campaign, ammonia emissions were substantially lower at both the primary absorber and secondary stripper whereas, formaldehyde emissions were considerably higher at the secondary stripper. Although actual air emissions were higher than estimated, the relatively small amount of emissions should not adversely impact surrounding terrestrial or water resources, since they would have been readily diluted and dispersed from the main exhaust stack at the E.W. Brown Generating Station.

5.2.1 550 MWe PCCCS Potential Emissions

From SMG's evaluation, a 550 MWe PCCCS located at an existing coal-fired steam electric plant would trigger a PSD review that would likely require the source to install best available control technology (BACT) for VOC emissions. If the system were installed within a Nonattainment Area for VOCs, the project would also be subject to the Nonattainment New Source Review (NA-NSR) program. The NA-NSR program requires a source to apply the lowest achievable emission rate (LAER) technology. BACT or LAER control measures for VOC emissions can add significant costs to the installation and operation of a 550 MWe PCCCS. The permitting procedure for a source undergoing PSD or NA review will require a minimum of 1.5 – 2.5 years for regulatory approval before construction.

Potential air emissions for a 550 MWe PCCCS were extrapolated from calculations and test data provided for the 0.7 MWe pilot plant at the E.W. Brown Generating Station. Although the precise method of solvent delivery and storage were unknown, estimated air emissions would be minimal compared to the project's overall potential emissions. However, further evaluation of emissions generated from bulk delivery and transportation of process solvents should be conducted when primary and secondary delivery methods (i.e., rail car or tanker truck deliveries) are known. Vapor recovery systems may need to be considered.

Most air emissions were emitted from the exit gas streams of the primary absorber (presuming secondary air stripper emissions are directed to the boiler). At this emission point, ammonia, process solvent and other solvent degradation products (e.g. - acetic acid) will likely be emitted in quantities requiring emission controls. Potential emissions for solvent degradation products exceed 1,500 tons per year, with ammonia emissions being the largest component (about 1,270 tons per year).

Further evaluation of the specific design and operating scenarios of a 550 MWe PCCCS is recommended to make a more accurate determination of human health and environmental impacts from air emissions. While the extrapolation methods used in this assessment are useful to estimate order-of-magnitude impacts; specific process data for gas flow rates, solvent liquid flow rates, stack parameters (height, diameter, gas velocity), and flue gas composition are needed to accurately quantify risks/impacts to human health or the environment.

5.3 Water/Wastewater Management

The project construction area was approximately 0.25 acres in size and located on existing, disturbed industrial property. Due to its relatively small footprint and location on an existing industrial site, the pilot project did not require a construction permit for storm water discharges. Depending upon the location, a larger scale facility will likely require a permit and storm water pollution plan implemented prior to construction.

Non-contact cooling water was required for the cooling tower. Make up water was required for the CO_2 absorber and pretreatment tower. Since the water demand for this system was minor relative to the amount of water required to operate the power station, make up water was obtained from E.W. Brown's permitted water intake. Therefore, no additional permitting for, or acquisition of, make up water was required. A larger scale facility will require a greater amount of water. The source of water will need to be evaluated to determine sufficient quantity and quality as well as associated environmental permitting requirements.

Process wastewater volumes were relatively minor and primarily generated from the pretreatment tower. Wastewaters were pumped to a wet flue gas desulfurization (WFGD) unit on site as a supplement water source and was not discharged or disposed on site. Due to the wastewater volumes, contaminant concentrations and ultimate disposal method, wastewater management was not a significant environmental concern. Increased wastewater volumes and constituent concentrations for a larger scale facility will need further evaluation to determine appropriate disposal methods. Recent changes in steam electric power generating effluent guidelines published by the EPA (40 CFR Part 423) will need to be considered to determine any required treatment requirements for surface discharges.

5.4 Waste Management

From information obtained from UKy-CAER, the primary wastes generated during the pilot test are identified below:

- Primary Stripper Reclaimer Sludge – 888 gallons;
- Spent MEA – 1,214 gallons;
- Spent H3-1 – 1,265 gallons;
- Absorber Column Wash Out – 6,500 gallons;
- Spent Desiccant - 138 gallons;
- Foundation wastewater – 1,684 gallons;
- Heat Exchanger Wash Out – 640 gallons;
- Used Activated Carbon – 440 pounds; and
- Waste Lubricants - < 20 gallons

As expected, most wastes were not characterized as a hazardous waste and were approved for disposal off site. No RCRA F, K, P, or U listed wastes were generated and no ignitable, corrosive or reactive hazardous wastes were generated. The one anomaly, was the spent H3-1 solvent, which was characterized as a toxic hazardous waste due to the presence of selenium above the regulatory threshold of 1.0 mg/l.

The types of wastes generated are not unusual for a large industrial facility, and do not represent a uniquely hazardous concern when managed properly. Solid and hazardous were characterized and disposed off-site at permitted waste disposal facilities.

The amount of waste generated by a larger scale facility will increase with the size of the facility, but likely economies of scale should enable the increase to be less than directly proportional to the size increase. Unless further testing of H3-1 is contemplated, site registration and management practices should not be substantially affected to be an unreasonable impact on operations, though waste disposal costs may increase.

5.5 Employee Hazards

The primary health hazards from raw material handling were derived from the CO_2 scrubbing solvents (MEA and H3-1) being identified as corrosive and irritants. Both solvents were mixed with water, which reduced the hazard, but use of appropriate PPE by employees was required to minimize these hazards. The remaining raw materials (e.g., sodium carbonate, calcium chloride and minor amounts of maintenance items) did not represent substantial health concerns, when appropriate precautions were used to avoid accidents and injuries. Safety hazards included potential exposure to noise, heat, steam and pressure vessels, but these are not unusual for an industrial facility and can be managed with appropriate precautions to avoid accidents and injuries.

As noted in **Section 5.1**, potential researcher exposures to nitrosamines during operation of the pilot plant may exceed USEPA acceptable risk ranges. However, uncertainties of the risk characterization suggest additional assessment of actual exposure frequencies, durations and EPCs for nitrosamines is warranted for the pilot scale as well as any larger scale project.

5.6 Community Impacts

The proposed project occupied a small portion of the E.W. Brown Generating Station. Raw material receipt and consumption are minor relative to quantities used by the power plant, as was construction and operating employee traffic. Due to its size, types of activities, limited use of chemicals and location within the E.W. Brown plant site, no significant adverse community impacts were identified for operation of the proposed pilot plant.

Implementation of a larger scale facility will need further evaluation with respect to potential air emissions, including quantifying specific nitrosamine compounds and evaluating the need for additional air emission control devices.

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SUPPLEMENTAL
ENVIRONMENTAL, HEALTH AND SAFETY ASSESSMENT APPLICATION OF A HEAT INTEGRATED, POST-COMBUSTION CO_2 CAPTURE SYSTEM MODIFIED WITH ADDITIONAL AIR EMISSION CONTROL USING A PROPRIETARY AMINE SOLVENT AT THE E. W. BROWN COAL-FIRED POWER PLANT HARRODSBURG, KENTUCKY

Preliminary Scientific/Technical Report

Reporting Period Start Date: July 1, 2019

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DISCLAIMER

ABSTRACT

In 2017, an Environmental Health and Safety (EH&S) Assessment was completed for operation of a pilot scale carbon dioxide (CO_2) capture system (CCS) at the Louisville Gas & Electric (LG&E) and Kentucky Utilities (KU) Energy, LLC (LG&E-KU) E. W. Brown Generating Station in Harrodsburg, Mercer County, Kentucky (SMG, 2017). A supplemental EH&S assessment was completed in March 2020 that evaluated the impact of changes made to the pilot CCS to address recommendations made in the 2017 EH&S report.

Most potential EH&S issues identified in 2017 are commonly found and successfully managed at large industrial facilities. No risks were identified that could not be successfully managed or would likely prevent implementation or environmental permitting of the pilot or larger scale plant. Potential health risks from exposure to low concentrations of nitrosamines were identified, but they could not be fully evaluated or confirmed. It was suggested that additional air emission control measures may be necessary for a larger scale system to reduce potential site worker health risks and possibly community risks.

In an effort to evaluate measures to reduce amine and related degradation compounds in air emissions and associated potential risks, the University of Kentucky Center for Applied Energy Research (UKy-CAER) designed and installed additional emission control systems at the CO_2 absorber tower exhaust. These additional controls were installed late spring 2019. Air emission testing from the absorber before and after the additional controls was conducted in 2019. Operation of the modified system with a proprietary amine solvent demonstrated a substantial reduction in amine related emissions and a moderate decrease in ammonia emissions from the absorber.

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Appendix A 2019 Test Campaign Results

LIST OF ACRONYMS AND ABBREVIATIONS

ACFM	Actual Cubic Feet per Minute
ACGIH	American Conference of Governmental Industrial Hygienists
BACT	Best Available Control Technology
CAA	Clean Air Act
CAP	Criteria Air Pollutant
CFR	U.S. Code of Federal Regulations
CO_2	Carbon Dioxide
CCS	Carbon Capture System
CMRG	Carbon Management Research Group
DOE/NETL	U.S. Department of Energy, National Energy Technology Laboratory
EH&S	Environmental Health & Safety
EPRI	Electric Power Research Institute
EWB	EW Brown (Generating Station)
ESSL	Exposure Specific Screening Levels
HAP	Hazardous Air Pollutant
IA	Insignificant Activity (as regulated under the Clean Air Act and related Kentucky regulations)
IARC	International Agency for Research on Cancer
IRIS	USEPA Integrated Risk Information System
KAR	Kentucky Administrative Regulation
kg	Kilogram
kg/d	Kilogram per day
kg/h	Kilogram per hour
KU	Kentucky Utilities
LAER	Lowest Achievable Emission Rate
LG&E	Louisville Gas & Electric
LoD	Level of Detection
MDL	Method Detection Limit
mg/L	Milligram per liter
MWe	Megawatt-electric power
MWth	Megawatt-thermal power
µg/L	Microgram per liter
NAAQS	National Ambient Air Quality Standard
NA-NSR	Nonattainment New Source Review
NDBA	N-Nitroso-n-butylamine
NDEA	N-Nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine

LIST OF ACRONYMS AND ABBREVIATIONS

NMEA	N-Nitrosomethylethylamine
NILU	Norwegian Institute for Air Research
NPIP	N-Nitrosopiperidine
NPY	N-Nitrosopyrrolidine
NSPS	New Source Performance Standard
NSR	New Source Review
OSHA	U.S. Occupational Safety and Health Administration
PCCCS	Post-Combustion CO_2 Capture System
PEL	Permissible Exposure Limit
PM_{10}	Particulate Matter less than 10 micrometers in diameter
PPE	Personal Protective Equipment
PSD	Prevention of Significant Deterioration
PTE	Potential-to-Emit
R&D	Research and Development
RAGS	Risk Assessment Guidance for Superfund
RAP	Regulated Air Pollutant
RCRA	Resource Conservation and Recovery Act
RSL	Regional Screening Level
SCMH	Standard Cubic Meters per Hour
SER	Significant Emission Rate
TLV	Threshold Limit Value
UKy-CAER	University of Kentucky Center for Applied Energy Research
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WFGD	Wet Flue Gas Desulfurization Unit

EXECUTIVE SUMMARY

This supplemental EH&S assessment addresses modifications to a pilot-scale, post-combustion CO_2 capture system (PCCCS) installed at the E.W. Brown coal-fired electric generating plant in Harrodsburg, Kentucky. The assessment was funded by a grant from the U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL) (Project Number DE-FE0007395).

The PCCCS included a packed column CO_2 absorber using a proprietary amine solvent; two packed-bed strippers with reboiler and reclaimer and a variety of support equipment. The modification included installation of a water wash scrubber system on the CO_2 absorber tower with an activated carbon bed system to remove accumulated organic compounds in the water wash solution. No additional controls were added to the solvent stripping columns. The objective was to evaluate the performance of the additional air emission control equipment and determine any affect upon previously identified environmental, health or safety concerns (SMG, 2017). The evaluation was based upon test results obtained in August and September 2019. The objective also included evaluation of potential impact upon environmental permitting of a larger scale (500 MWe) PCCCS.

The scope of the assessment was limited to evaluating process design plans, process operation and testing information provided by the University of Kentucky Center for Applied Energy Research (UKy-CAER). Process design and operation information included: process flow diagrams; operating parameters; raw material consumption rates; and air emissions testing.

A summary of the findings from the 2017 EH&S report and pilot testing is provided below.

- Direct contact with the amine solvent was the primary employee health hazard from raw material handling, since it is classified as corrosive and an irritant in concentrated form. These hazards are readily mitigated by avoiding exposure to solvent by using appropriate personal protective equipment (PPE). Similarly, safety hazards that included potential exposure to noise, heat, steam and pressure vessels were not unusual for an industrial facility and managed with appropriate precautions and PPE to avoid accidents and injuries.

- Using monoethanolamine (MEA) and Hitachi H3-1 as the capture solvents, the maximum detected concentration for ammonia at the primary absorber and secondary stripper exhausts exceeded the United States Environmental Protection Agency (USEPA) Regional Screening Level (RSL) for inhalation and occupational exposures levels published by the federal Occupational Health and Safety Administration (OSHA Permissible Exposure Level (PEL) and American Conference of Governmental Industrial Hygienists (ACGIH Threshold Limit Value (TLV). Detected concentrations exceeding occupational exposures do not necessarily indicate a cause for employee exposure concern, since employees would not be exposed to air emissions from the primary absorber and secondary stripper for 8 hours per day, 5 days per week over a lifetime work duration of 30 years (basis for determining PELs). Similarly, concentrations detected above USEPA RSLs do not necessarily indicate a community concern for ambient air quality due to the emissions being diluted in the exhaust stack for the generating station.

- Elevated concentrations of ammonia, MEA and possibly formaldehyde detected at the secondary stripper and extrapolated to a large-scale facility warrants additional evaluation and consideration of additional emission control measures, if the exit gas stream from the secondary stripper were not directed to a boiler and used for combustion air.

- Formation of nitrosamines may occur from the degradation of the amine solvent. Although nitrosamines were not detected in air emissions or used solvent, the Levels of Detection (LoDs) were not low enough to fully evaluate potential health effects if they were present. Assessment of potential exposures to nitrosamines using assumptions based upon limited data indicates that researcher exposure levels may exceed USEPA acceptable cancer risk ranges of 1E-06 to 1E-04. Additional assessment of actual exposure frequencies, durations and concentrations of specific nitrosamine isomers at lower detection levels is warranted to better characterize potential health risks.

Due to the use of a different amine solvent in 2019 as well as improvements in process management and monitoring methodology utilized since the 2017 report, it was determined that comparison of recent results with prior test results may not be valid with respect to evaluation of the additional system control measures. Therefore, this evaluation focused solely on comparison of 2019 sample results from the absorber before and after the added water wash system. The results demonstrate substantial reduction in amine emissions, and presumably some amine related degradation compounds. Values detected at the water wash exit were generally at least an order of magnitude less and the average amine values detected (on a ppmV basis) at the water wash exit were about 95% less.

Comparison of ammonia emissions from the absorber and after the water wash demonstrate a reduction in the average concentration of about 13.7%; however, the ranges in ammonia detected did not vary by much.

From an employee health perspective, ammonia was consistently detected above the industrial inhalation noncancer Risk Screening Level (RSL) of 2,200 ug/m^3. Exceedance of the RSL indicates a potential health risk that will need to be managed with appropriate PPE.

No nitrosamine compounds were detected at the improved levels of detection (LoDs), which were generally an order of magnitude lower than the prior campaign. However, if nitrosamine compounds were present at concentrations half of the new LoDs, there would still be a potential employee exposure concern. Evaluation of detectable nitrosamine compounds in any carbon polishing waste, recirculated amine solvent and reboiler sludge is also recommended to determine potential human hazards from exposure to waste management and identify any new protective measures to be deployed.

From a community impact perspective, if nitrosamines were present in the absorber exhaust stream at half of the new LoDs, they would be 2-3 orders of magnitude higher than a generally recognized acceptable lifetime ambient air exposure value of 3 ng/m^3. Depending upon the stack height and local topography and meteorological conditions, air dispersion may reduce ground level exposures of the community to levels below this acceptable lifetime value.

Due to uncertainties in the exposure scenarios considered and data generated, extrapolating these results to operation of a large scale PCCCS may not accurately identify potential risks of nitrosamine exposure by site workers or the surrounding community. However, it is reasonable to presume that a larger scale facility will consume greater amounts of solvent that, depending upon the solvent formulation, may generate larger amounts of nitrosamines, albeit at similar concentrations with increased air flow, that could result in greater risk of exposure and harmful health effects without additional emission control measures.

Extrapolating data obtained from the pilot plant testing suggests that a larger scale (550 MWe) PCCCS located at an existing coal-fired steam electric plant would trigger a Prevention of Significant Deterioration (PSD) review, likely requiring installation of best available control technology (BACT) for VOC emissions. If the system were installed within a Nonattainment Area for VOCs, the project would also be subject to the Nonattainment New Source Review (NA-NSR) program that requires application of the lowest achievable emission rate (LAER) technology. BACT or LAER control measures for VOC emissions can add significant costs to the installation and operation of a 550 MWe PCCCS and the plausible permitting procedure could require a minimum of 1.5 – 2.5 years for approval prior to commencing construction.

1.0 INTRODUCTION/BACKGROUND

1.1 Project Funding and Description

The project consists of design, installation and evaluation of a ceramic membrane system and add-on air emission controls for a pilot scale post-combustion CO_2 capture system (PCCCS) located at the coal fired E. W. Brown Generating Station at Harrodsburg, Kentucky (see **Figure 1 Site Location Map, Figure 2 Site Vicinity Map** and **Figure 3 CCS Slipstream Location**). The project was funded by grants from the U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL Project Number DE-FE0007395), the Carbon Management Research Group (CMRG, a utility group comprised of Duke Energy, American Electric Power, East Kentucky Power, Electric Power Research Institute (EPRI), LG&E/KU and the Kentucky Department for Energy Development and Independence.

1.2 Project Purpose and Objectives

The purpose of the project was to evaluate improvements in CO_2 capture and recovery through use of a membrane system and evaluation of the performance of additional air emission controls installed on the CO_2 absorber column and the associated affects upon potential EH&S concerns identified in a prior report (SMG, 2017).

1.3 EH&S Evaluation Process and Objectives

Process design and operation information was obtained from the UKy-CAER. This information included process flow diagrams, operating parameters, and measured air emissions at the absorber exit and after the water wash system added to the absorber. The pilot plant was designed to operate at a 0.7 MWe (2 MWth) scale (~13.7 tonnes per day CO_2) receiving a slipstream flow of approximately 2340 SCMH (1400 cfm) from the E.W. Brown combined exhaust stream, after the wet flue gas desulfurization (WFGD) system. Testing and evaluation of the additional controls for this report was completed in August and September 2019.

The objective of this evaluation was to determine the effectiveness of the additional air emission controls for the absorber and their impact upon related potential EH&S concerns identified previously (SMG, 2017).

2.0 SITE DESCRIPTION

2.1 Location

The E.W. Brown Generating Station is located at 815 Dix Dam Road in Harrodsburg, Mercer County, Kentucky. It is located approximately 7 miles north/northeast of Harrodsburg, Kentucky and 9 miles southwest of Nicholasville, Kentucky. Approximate latitude and longitude are: 37° 47’ 21” north, 84° 42’ 55” west. Approximate elevation is 890 feet above mean sea level. A Site Location Map has been included as **Figure 1** in this report.

2.2 Site Land Use

Site land use is industrial within an existing power generating station. The footprint for the power plant contains greater than 20 acres and includes a hydroelectric plant, three coal-fired generating units, six combustion turbines and associated raw material and fly ash handling operations.

Site land use was not altered or adversely affected by the pilot project or the additional air emission control. The project footprint was less than 0.25 acre and located entirely within the existing station footprint. Project equipment was installed next to an existing building. Researchers were on site to operate the pilot plant and perform continuous emission monitoring activities. EPRI also had a laboratory to conduct independent sampling at the host site. Existing roads and parking areas were utilized. Traffic followed existing roads within the power plant and no new right of ways were required or disturbed by the project.

2.3 Adjacent Land Use

No local, state or federal parks, forests, monuments, scenic waterways, wilderness or tribal lands are located near the project site. The power plant is located near Herrington Lake, which is used for recreational purposes as well as the water supply for the hydroelectric plant and coal-fired power units. The lake is approximately 1,100 feet south/southeast of the pilot project work area (reference **Figure 2).**

2.4 Cultural, Recreational and Environmentally Sensitive Features

According to the Harrodsburg/Mercer County Tourist Commission, Herrington Lake is a 3,600-acre lake popular for many outdoor recreational activities. The lake was created by construction of a dam across the Dix River. Herrington Lake is about 35 miles long, up to 1,200 ft. wide and has over 325 miles of shoreline. The deepest area is near Dix Dam where water depth reaches 249 feet. The estimated capacity of the lake is 175,000,000,000 gallons.

Dix River Dam (Structure ID No. 88003384) is listed on the National Register of Historic Places. It was added to in 1990 for its historic significance in architecture and engineering design.

The pilot project was a relatively small facility located on the grounds of the existing E.W. Brown power plant, isolated from Herrington Lake and Dix River Dam. The pilot project did not have any adverse impact on either of these resources.

3.0 PROCESS DESCRIPTION

3.1 E. W. Brown Generating Station Description and Tie-In

E.W. Brown Generating Station was the host site for the pilot plant and related equipment. The pilot project was located with accessible proximity to the flue gas duct work, electrical and water utilities without impacting resource demand for the host utility. The flue gas slipstream was collected after the WFGD unit. Pilot project effluent was re-injected into the flue gas in adjacent ports after the WFGD unit (refer to **Figure 3**).

3.2 UKy-CAER Unit Description and Process Flow

The pilot PCCCS included the operation of a series of process vessels (tanks and columns) and their support equipment to remove impurities and CO_2 from the flue gas. Process flow through the original system consisted of a flue gas slipstream initially directed to a pretreatment tower to remove sulfur and reduce other impurities by using a sodium carbonate (soda ash) solution. Following pretreatment, flue gas enters the CO_2 absorber column containing an amine scrubber solution. CO_2 in the flue gas is absorbed into the liquid amine solution, causing the solution to be rich in CO_2. The CO_2 rich amine solution is directed to two strippers to remove CO_2 from the solution, which is then returned to the absorber. A reclaimer and reboiler are support units to the stripping process that facilitate reconditioning of the solvent for return to the absorber. The scrubbed gas stream exiting the absorber column is re-injected to the power plant flue gas after the WFGD. Exhaust from the stripper columns can be directed to the pretreatment tower and to the power plant flue gas after the WFGD.

For this assessment, additional equipment was added to improve performance of the system. The additional equipment included a ceramic membrane unit added between the pretreatment tower and the absorber to concentrate CO_2 from approximately 14% to a potential 20% for improved recovery efficiency.

To provide additional control for one of the main sources of amine air emissions, UKy-CAER designed and installed a closed-loop, water-wash scrubber at the absorber outlet. The scrubber has structured packing and a demister. The scrubber is equipped with a liquid level sensor to prevent flooding and drains to the amine absorber. Integrated with this scrubber is an activated carbon absorber that periodically is used to collect and remove captured impurities in the water wash solution. A diagram portraying the CCC with this additional equipment is provided in **Figure 4**.

Slipstream process inputs for the pilot plant were similar to prior testing, with exception of amine consumption being reduced to almost 10 % of prior use due to the use of the water wash system. Approximate inputs are identified in **Table 1** below.

Table 1
PCCCS Raw Material Inputs

Raw Material Input	Planned Rate
Proprietary Amine Solvent	0.21 kg/d
Flue gas stream entering slipstream	1,400 SCFM
Sodium Carbonate solid	50.5 kg/d
Water (non-contact cooling makeup intake)	33,600 kg/d (1400 kg/h)
Water (cooling water process recirculation)	7,680 kg/d (320 kg/h)

kg/h = kilograms per hour

kg/d = kilograms per day

SCFM = standard cubic feet per minute

4.0 EH&S EVALUATION

4.1 Solvent and Degradation Products Risk

4.1.1 Introduction

Evaluations were previously conducted of the qualitative and quantitative health risks related to CO_2 capture and storage using amine solvents to remove CO_2 from post-combustion flue gas (ENRISQ, LLC, February 2013; ENRISQ, LLC; February 2016). These were performed to support an initial CO_2 capture pilot testing program, and subsequent additional larger-scale testing scenarios and testing of various amine-based CO_2 capture solvents.

The evaluations concluded that MEA and proprietary amine solvents pose little human health or ecological risk when proper safety, handling, and industrial hygiene procedures are followed. The solvents may cause irritation to eyes, skin, or respiratory system if direct contact is allowed to occur.

It was also concluded that if nitrosamines are formed as degradation products of the CO_2 capture solvents, they may pose significant human health and ecological risks if exposures are allowed to occur.

In addition to installation of a water wash scrubbing system to the absorber outlet, the CO_2 capture solvent testing process has improved with a more robust analytical methodology to achieve significantly lower levels of detection for nitrosamine degradation products. This supplemental risk evaluation assessed the effectiveness of the lower detection levels in characterizing potential human health risks associated with nitrosamines generated during the 2019 testing and sampling process conducted at the E.W. Brown facility.

4.1.2 Methods, Materials, Toxicity and Exposure Assessment

Methodology used to conduct this risk evaluation is consistent with the Risk Assessment Guidance for Superfund (RAGS) developed by the USEPA, and generally accepted toxicological and risk assessment practices. The evaluation focused on potential health risks related to possible direct exposures to the proprietary amine solvent, ammonia and nitrosamines analyzed using the lower LoD methodology during the 2019 testing at the E.W. Brown facility. Project related materials, documents, sampling data, and sampling protocol information were provided by UKy-CAER. Additional standard resources such as the USEPA Regional Screening Levels Summary Table (USEPA, November 2019 - verified March 2020), and other standard toxicological information resources were used to evaluate potential health risks.

Materials and documents provided by UKy-CAER and used in this risk evaluation were:

- Summary Table of Sampling Results and Levels of Detection for August 2019 sampling events.
- Summary Table of Daily Run Times with total run hours.
- Summary of Sampling Methodology and Protocol provided on February 27, 2020.

Calculations were made based on theoretical potential exposures during testing sessions based on run times presented in the Daily Run Times summary table. Calculations followed, and were consistent with, RAGS methodology and generally accepted toxicological and risk assessment practices. Information on the potential exposure duration and frequency was provided by the UKy-CAER team and based on the previous evaluations of exposures. Since specific data and information (i.e., measured ambient air concentrations) for actual personnel exposures were not available, extrapolations were made from available information and previous analyses. Specific quantitative toxicity values, and risk-based screening concentrations for ammonia and the nitrosamines are available from the USEPA (USEPA RSLs, November 2019). There is no RSL available for a generic “amine”.

Pilot system testing was conducted in July, August, September and October for a total of thirty days in 2019. The daily run time ranged from five hours to fourteen hours per day. The total run time, including pre-modification run hours was 512 hours (273 hours with modifications).

Sampling for ammonia and amine (due to the proprietary nature of the amine solvent, no specific amine compounds were analyzed) was completed on August 6, 7, 8, 13, 15, and September 13. Samples were collected from the Absorber Exit and the Water Wash Exit. The primary health concern identified for the amine-type CO_2 capture solvent is the corrosive nature of the material. Direct exposure to the solvents may cause severe skin irritation, damage to the eyes, mouth, throat, and respiratory system. Some of the compounds may also cause allergic reactions and a few have been identified as reproductive toxins. If these exposures are prevented through proper process and sampling technique, the use of personal protection equipment (PPE), and proper engineering controls, then the corrosive nature and other toxicities of the solvents will be mitigated.

Samples for nitrosamines were collected on two occasions on August 14, and only from the Water Wash Exit. The longest duration of any sampling event for nitrosamine analysis was 145.41 minutes. No analyzed nitrosamine compound was detected at the current lowest level of detection. As such, this evaluation is qualitative, or semi-quantitative, and does not provide a specific point-estimate of a risk level. A health concern for nitrosamines is the potential cancer risk from exposure to nitrosamines that may be derived from the used solvents. The Integrated Risk Information System (USEPA, 1987) identifies many nitrosamines as Group B2 (probable human carcinogens) and the U.S. Department of Health and Human Services (2016) identifies them as reasonably anticipated human carcinogens. Nitrosamines are considered to pose a potential cancer risk even at very low levels of exposure.

While direct exposures to the solvents may be prevented with appropriate PPE and work practices, the formation of nitrosamines from the solvents during the CO_2 capture process, and the presence of nitrosamines in the bulk solvent may be problematic. Inhalation exposures to nitrosamines in ambient air or during process sampling may pose a cancer risk to study workers. These risks may be present at very low levels of exposure, even at the parts-per-trillion (ppt) concentration level of exposure.

A complete exposure assessment quantifies the potential level(s) of exposure to specific compounds and their environmental concentration(s). Exposures may occur through inhalation, dermal contact, and/or ingestion. Ingestion of compounds in an environmental exposure scenario is usually considered to be unintentional and is classified as incidental ingestion. For purposes of this evaluation, incidental ingestion of materials related to the CO_2 capture study are considered to be negligible and are not further evaluated. Based on discussions with UKy-CAER members and confirmed by the recent email describing sampling protocol, appropriate personal protection equipment (PPE) such as safety glasses, laboratory coats, and chemical-resistant gloves were used, and a respirator was available and used during sampling. A fume hood and chemical-resistant gloves were used during sample preparation. Therefore, dermal exposures are also considered to be negligible. Inhalation is the primary route of potential exposure evaluated in this assessment.

Toxicity information and risk-based screening concentrations for inhalation exposures were obtained from the USEPA Regional Screening Level (RSL) Summary Table (November 2019, verified March 2020). The 2019 testing protocol included the analysis of ammonia, amine, and seven nitrosamines: N-nitrosopiperidine (NPIP), N-nitrosodimethlyamine (NDMA), N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), nitrosodi-n-propylamine (NDPA), N-nitrosopyrrolidine (NPY) and N-nitroso-n-butylamine (NDBA). Of these constituents, only ammonia and amine were quantified above the respective level of detection (see **Appendix A, 2019 Test Campaign Results**). Because there is no RSL for a generic amine compound, it was not evaluated further in this risk characterization.

4.1.3 Risk Characterization

Risk characterization integrates the toxicity of a compound with the opportunity or level of exposure to estimate the level of human health or ecological risks related to exposures to the compound. As described above, inhalation was considered the primary route of potential exposure for the constituents analyzed. Ammonia was detected in all of the samples collected during the test run. The industrial inhalation RSL for ammonia is 2,200 ug/m^3 based on a noncancer health risk. All of the sample concentrations of ammonia (average for absorber exit – 13,350.58 ug/m^3; average for water wash exit = 11,979.20 ug/m^3) exceed the RSL for a full-time industrial worker exposure scenario. Exceedance of the RSL indicates a potential health risk.

The primary risk evaluated is potential cancer risk as a result of inhalation of nitrosamines. The risk characterization calculations evaluated the "worst-case" scenario. That is the maximum level of exposure to the maximum concentration of nitrosamines. Because the 2019 testing did not detect any of the nitrosamine compounds above the level of detection, a value of one half of the lowest detection level for the individual compounds was used as a surrogate concentration for the exposure concentration for the risk characterization. This concentration value was compound-specific and varied between the individual nitrosamines. These values were compared to the appropriate USEPA RSL to provide a "worst-case" exposure scenario and risk characterization.

The RSLs are based on a full-time industrial worker exposure scenario. These screening risk levels assume workplace exposures occurring 8 hours per day, 250 days per year for 25 years or 50,000 hours of exposure through inhalation. This assumption greatly exaggerates the potential exposure to the Absorber Exit or Water Wash Exit materials. Actual exposures to monitored constituents in the system would be expected to be much less and occur only during sampling events or work on the test system.

The individual nitrosamine congeners, their respective Regional Screening Level for industrial inhalation exposures and one half of the value of their respective lowest level of detection (1/2 LOD ng/m^3) are presented in the following summary table. It should be noted that the concentration units have been converted from ug/m^3 as used in the sample results tables to ng/m^3 for ease of reading and comparison.

Table 2
Nitrosamine Risk Characterization Summary

Constituent	RSL ng/m^3	½ LOD ng/m^3	Risk Level*
NPIP	4.5	84.7	18.8E-6
NDMA	0.88	122.2	138.9E-6
NMEA	1.9	152.7	80.4E-6
NDEA	0.29	129.0	444.8E-6
NDPA	6.1	87.8	14.4E-6
NDY	20.0	204.9	10.2E-6
NDBA	7.7	296.8	38.5E-6

* Risk Level is theoretical cancer risk level at full exposure.

As shown in **Table 2,** one half of the lowest respective detection level is an order of magnitude or more than the respective RSL for an industrial worker exposed for a full work-life. This indicates that even though no nitrosamines were detected in the samples, it can’t be ruled out that nitrosamines are not present in concentrations that may pose an unacceptable risk if a full exposure scenario of 50,000 hours occurs.

Use of PPE will result in negligible direct (dermal) exposures to liquid and based on sampling protocols, actual inhalation exposures are expected to be negligible. Since the total pilot system test run was 512 hours (not the 50,000 hours of a full work-life used for the RSL), personnel exposure during the test run would be equivalent to 0.01 of the full work-life basis. This reduced exposure may not result in an unacceptable risk level, depending on actual concentrations of the individual nitrosamine compounds present.

Exposures that may have occurred would have been most likely during the sampling procedure and sample handling. The longest sampling time was 145.41 minutes (approximately 2.42 hours) or approximately 0.00005 (2.42/50,000) of the 50,000-hour full exposure scenario used to calculate the RSLs. This was also less exposure time than occurred during the study conducted in 2016 (56 hours). It is unlikely that the short duration of exposure during the 2019 sampling would result in a significant cancer risk level from exposure to possible nitrosamines in the Water Wash Exit material.

In order to provide a quantitative evaluation, the specific exposure time for this round of testing was used to calculate adjusted screening levels for comparison to the levels of detection. The RSLs for a full-time worker exposure based on 50,000 hours were multiplied by 20,000, the factor of decrease in exposure time (1/0.0005). Using this factor, the adjusted exposure specific screening levels (ESSLs) for the 2019 testing are summarized in the following Table.

Table 3
Nitrosamine Specific Exposure Scenarios

Constituent	ESSL ng/m^3	½ LOD ng/m^3	Risk Level*
NPIP	90E+3	84.7	9.4E-10
NDMA	17.6E+3	122.2	6.9E-9
NMEA	38E+3	152.7	4.0E-9
NDEA	5.8E+3	129.0	2.2E-8
NDPA	122E+3	87.8	7.2E-10
NDY	400E+3	204.9	5.1E-10
NDBA	154E+3	296.8	1.9E-9

ESSLs are 20,000 times greater than the USEPA RSLs

* Risk Level is theoretical cancer risk level.

As shown in the **Table 3**, the greatly reduced level of exposure significantly reduces the potential cancer risk below regulatory guidelines of 1x10E-04 to 1x10 E-06. It should be noted that this is a theoretical extrapolation and may not reflect actual risks if such exposures were to occur. Proper use of appropriate PPE is still recommended.

4.1.4 Risk Conclusions

Due to possible irritation and other toxicities, direct exposure to amine-based CO_2 capture solvents should be avoided and appropriate PPE used. Exposures to ammonia in the Absorber Exit and Water Wash Exit material should be avoided, and appropriate PPE employed.

In addition, formation of nitrosamines may occur from the degradation of the solvents during the CO_2 capture process. Nitrosamines are considered potent human carcinogens. The UKy-CAER has developed an improved testing methodology for analyzing nitrosamine congeners with a lower level of detection. Nitrosamine analysis was conducted on a limited number of samples (August 14, 2019) with no nitrosamine compounds detected. Improved sample and analysis techniques yielded levels of detection (LoD) generally an order of magnitude lower than the prior campaign in 2015. Although the methodology has been improved, even one half of the lower levels of detection are still at least ten times greater, and in some instances, orders of magnitude greater than the respective EPA RSLs for a full work-life industrial inhalation exposure scenario. The results do indicate, however, that the relatively low run time of the pilot system test, and the actual sampling time would not result in significant levels of exposure to possible nitrosamines.

4.2 Air Emissions

Additional air emission control equipment for the absorber had no direct impact upon emissions from storage of raw materials discussed in the prior May 2017 EH&S report. The types and quantities of raw materials stored on site and associated air emissions were no different than previously evaluated. There was no further evaluation of materials stored on site with respect to potential air emissions at the pilot scale. Anticipated emissions for a larger scale facility should be no different than previously described.

This evaluation considered additional control for emissions of the 0.7 MWe PCCCS located at the E.W. Brown facility and potential emissions of a proposed 550 MWe PCCCS. Ammonia and amine were the indicator parameters used to evaluate the performance of the add-on controls. Comparison of recent sample results with those obtained in 2015 – 2016 and provided in the prior May 2017 EH&S report was not considered to be appropriate or necessarily informative due to improvements in process control that have been developed and gained through system operation, as well as differences in solvent amine composition and chemistry. Therefore, this evaluation primarily focuses on comparison of sample results from the absorber before and after the added water wash system.

4.2.1 0.7 MWe PCCCS Emissions, Impacts and Source Classification

Amine slip from the proprietary solvent and associated degradation compounds (e.g., ammonia) remain the largest contributors to atmospheric air emissions from the 0.7 MWe PCCCS. The sampling results in **Appendix A** demonstrate a substantial reduction in atmospheric emissions of amine, and presumably some amine related degradation compounds. The average amine values detected at the water wash exit were two orders of magnitude less than what was detected at the absorber exit (0.572 ppmV versus 10.49 ppmV), a reduction of almost 95% and the calculated mass emissions were an order of magnitude less (7,940 ug/m^3 versus 64,578 ug/m^3).

Ammonia emissions from the PCCCS absorber were also reduced by use of the add-on water wash system; however, not at a similar rate. The average reduction in ammonia concentration at the water wash exit gas stream was approximately 13.7%.

The previous conclusion that actual emissions from the 0.7 MWe PCCCS are not anticipated to adversely impact surrounding terrestrial or water resources remains unchanged.

The installation and operation of the 0.7 MWe PCCCS was submitted[1] and processed as an "*off-permit*" change pursuant to Section 17(1) of Title 401 Kentucky Administrative Regulation (KAR) 52:020. Criteria Air Pollutant (CAP) emissions from the 0.7 MWe PCCCS remain below Insignificant Activity (IA) emission thresholds and do not violate or affect any existing terms or conditions of the permit E.W. Brown Generating Station Title V Operating permit. Therefore, the source classification of the 0.7 MWe PCCCS as a non-major research and development activity collocated at Title V major source exempt from permitting or registration under 401 KAR 52:020, 401 KAR 52:030, 401 KAR 52:040, or 401 KAR 52:070 remains valid.

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1. Kentucky Utilities Company – E.W. Brown Generating Station submitted a letter "*Re: Kentucky Utilities/E.W. Brown Generating Station (AI #3148) Construction of Slipstream-scale* CO_2 *Capture System"* on March 25, 2014 to US EPA Region 4 and the Kentucky Division for Air Quality notifying the Administrators of proposed changes at the facility to install insignificant activities (0.7 MWe PCCCS) qualifying for processing as an off-permit change.

4.2.2 550 MWe PCCCS Emissions, Impacts and Source Classification

In the prior EH&S report (SMG, 2017), volumetric and gravimetric pollutant concentration data from emissions testing at the 0.7 MWe PCCCS (CB&I, March 2016 and UKy-CAER), extrapolated gas flow rates for a proposed 550 MWe PCCCS and AP-42 emission factors were used to develop potential-to-emit (PTE) calculations (i.e., 8,760 hours per year PCCCS operation at a “worst case” emission rate) for CAPs, Hazardous Air Pollutants (HAPs) and Regulated Air Pollutants (RAPs). Project PTE calculations for installation and operation of a 550 MWe PCCCS were shown to significantly exceed the PSD VOC Significant Emission Rate (SER) of 40 tons per year at 3,888 tons per year (SMG, 2017). While the improved process control and air emission controls show significant reductions in atmospheric amine emissions (88%) from the absorber at the 0.7 MWe PCCCS, a revised PTE for a 550 MWe PCCCS with an assumed 88% reduction in VOC emissions remains well above the PSD SER for VOCs.

The extrapolation methods used in the prior EH&S report remain useful to estimate order-of-magnitude environmental impacts and identify potential human health concerns from air emissions of a 550 MWe PCCCS. However, specific process data for gas flow rates, solvent liquid flow rates, stack parameters (height, diameter, gas velocity) and flue gas composition are necessary to accurately quantify risks/impacts to human health or the environment. A detailed evaluation of potential human health and environmental impacts from air emissions of a 550 MWe PCCCS is recommended in a future EH&S assessment once more process data is available.

As stated in the prior EH&S report, the installation and operation of a 550 MWe PCCCS would be a *Major Modification* at an *existing named source*[2] subject to federal permit review by EPA under the NSR permitting program. PCCCS process control improvements and use of an add-on water wash system significantly reduce calculated potential emissions; however, source-wide PTE totals for CAPs and RAPs remain above significant emission thresholds for air permitting (i.e., PSD VOC SER). Therefore, the conclusions presented in the prior EH&S report (SMG, 2017) are unchanged.

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[2] *Named sources* are stationary source categories listed in 40 CFR §51.166(b)(1) with a PTE of ≥ 100 tons per year (including fugitive emissions) for a regulated pollutant subject to EPA’s New Source Review program for construction of any new major stationary source or any project at an existing major stationary source in an area of attainment or unclassifiable under CAA sections 107(d)(1)(A(ii) or (iii).

At a minimum, the project would trigger federal review for PSD and require the source to determine the maximum degree of control for VOC emissions using a case-by-case BACT analysis (i.e., emission reductions that can be achieved considering energy, environmental and economic impacts). If the installation occurred at a source located in a Nonattainment area for one or more NAAQS, NA-NSR permitting requirements could subject PCCCS air emissions to EPA's most stringent control technology standard LAER (i.e., does not consider economic, energy, environmental or other factors when determining the lowest achievable emission rate) and require emission offsets prior to preconstruction permit approval.

A *Major Modification* at an *existing named source* subject to EPA approval under the NSR permitting program (PSD and/or NA-NSR) significantly increases preconstruction approval requirements for an air permit to install/operate a 550 MWe PCCCS. The length of the air permitting process for a project subject to the NSR program often takes at least 1.5 – 2.5 years for approval. Moreover, BACT or LAER control technology requirements for VOC emissions will likely add significant costs to the project.

4.3 Wastewater Management

Wastewater and captured amine compounds generated from the water wash system was directed to the absorber and recirculated in the absorber tower. There was no change in wastewater generation or management since the prior evaluation. Process wastewater of approximately 700 gallons per day from the pretreatment tower and non-contact cooling water blowdown of up to 80,000 gallons per day were pumped to the power plant WFGD as a water supplement. No collection, treatment or disposal was required. Wastewater management was not a significant environmental concern in the prior report and not evaluated further for this report.

4.4 Waste Management

A waste determination is required for each solid waste generated as part of the project. All solid wastes were disposed off site in strict accordance with applicable USEPA Resource, Conservation and Recovery Act (RCRA) requirements. The only new waste that will be generated is spent activated carbon used to polish the water wash system. Evaluation of hazardous waste characteristics will need to include testing for toxic metals, including selenium, arsenic and mercury.

As reported previously, most wastes were not characterized as a hazardous waste and were approved for disposal off site. No RCRA F, K, P, or U listed wastes were generated and no ignitable, corrosive or reactive hazardous wastes were generated. The one previous anomaly, was spent H3-1 solvent, which was characterized as a toxic hazardous waste due to the presence of selenium above the regulatory threshold of 1.0 mg/l. More frequent solvent reclamation may reduce the amount of selenium characteristic hazardous wastes generated, but it is unlikely they can be totally eliminated.

The types of wastes generated are not unusual for a large industrial facility, and do not represent a uniquely hazardous concern when managed properly. Solid and hazardous were characterized and disposed off-site at permitted waste disposal facilities.

The amount of waste generated by a larger scale facility will increase with the size of the facility, but likely economies of scale should enable the increase to be less than directly proportional to the size increase.

4.5 Employee Hazards

The E.W. Brown Generating Station is a power plant that presents a range of physical hazards to employees typical of industrial facilities. The site has a facility specific worker health and safety program. Employees working on the pilot project were required to adhere to the Station's worker safety programs, as well as any developed worker safety program specific to the proposed slipstream facility project.

Since there was no change in actual or types of raw materials used, the findings and conclusions of the prior assessment have not changed. The primary potential hazard was the amine solvents could cause acute or chronic health effects to employees. Improper material handling could potentially result in serious inhalation, dermal or ingestion hazards. Eyewash and safety showers were installed near storage and process areas.

Operation at a larger 500 MWe coal fired power generating station is not anticipated to add any new or significant source of employee hazard.

As noted in **Section 4.4,** the only new waste generated from the system will be activated carbon used to polish the water wash system. Evaluation of hazardous waste characteristics will need to include testing for toxic metals, including selenium, arsenic and mercury. Evaluation of detectable nitrosamine compounds in this waste, recirculated amine solvent and reboiler sludge is also recommended to determine potential human hazards from exposure to waste management and identify any new protective measures to be deployed.

4.6 Noise

Installation of the additional air emission controls for the absorber did not add a new, significant source of noise. Noise is primarily generated by process pumps and blowers. Internittent exposure to noise by site researchers was mitigated with appropriate hearing protection. Due to the size of the operation (relative to the E.W. Brown facility), noise generated at the pilot plant did not represent a significant concern on the property or to the surrounding community. Installation of a larger system at a 500 MWe coal fired power generating station is not anticipated to add any significant source of noise over existing operations.

4.7 Community Impacts

The addition of air emission controls on the absorber did not add substantially to the PCCCS footprint. No change in the prior assessment's evaluation, which identified no significant adverse community impacts from operation of the proposed pilot plant.

The added control reduced amine emissions from the absorber and would likely have reduced any potential nitrosamine emissions. Due to the sample analysis level of detection (LoD) achievable at this point, it is uncertain whether any nitrosamine emissions may represent a concern at this scale or at a much larger scale. No nitrosamine compound was detected at the improved LoDs developed by the UKy-CAER, which were all below ppb/V concentrations with calculated mass values all below 1 mg/m^3 (ranging from 169.4 ng/m^3 – 779.4 ng/m^3 – see **Appendix A**).

A generally recognized and often referenced acceptable air emission value for total nitrosamines (and nitramines) is 0.3 ng/m^3 developed by the Norwegian Institute of Public Health (NIPH, 2011), which would be 2-3 orders of magnitude lower than any nitrosamine that may be present at half the current LoD calculated mass value per mg^3. Lower detection levels would be required to make a valid comparison.

It should be noted that the NIPH acceptable level (at 1xE-06 risk of cancer) was extrapolated from acceptable drinking water levels and applied as a lifetime exposure to ambient air quality (at ground level) and a number of other acceptable ambient air levels have been proposed that range from 0.07 ng/m^3 – 10 ng/m^3 (SEPA, 2015). These acceptable risk levels all apply to human exposure over a lifetime. Actual values for emissions from any PCCCS would need to be quantified and ambient dispersion would need to be evaluated to accurately assess the risk of what a person on the ground would be exposed to over a lifetime.

It has been reported that photolysis can degrade or destroy nitrosamine compounds in the air over relatively short periods of time (Spietz, et al, 2017). This might suggest a higher “acceptable” air emission value at the exhaust stack with adequate air dispersion contributing to lower ground level concentrations and lower potential risk to the surrounding community.

4.8 Impact Mitigation Strategies

Potential employee exposures to hazardous chemicals were minimized with appropriate work practices and employee protective equipment. Concentrated forms of the solvents were identified as category 3 health hazards with serious acute hazards. Amine solvents in concentrated form have been associated with long term chronic hazards. Dilute concentrations used on site represented a lower hazard potential. Appropriate personal protective equipment was identified and required to be used to mitigate potential risks to employees.

Improvement in analytical testing techniques to reduce the LoD for nitrosamine compounds will need to be developed to accurately characterize potential health risks from employee or community exposure to potential nitrosamine compound generation.

4.9 Precautions and Accidental Release Measures

There were no changes in the type or quantities of materials used during this test campaign. The same general precautions and recommendations for spill response remain unchanged and are not atypical of any similar industrial workplace.

5.0 CONCLUSIONS AND RECOMMENDATIONS

This supplemental EH&S assessment was conducted to evaluate modifications to a pilot-scale, post-combustion CO_2 capture system (PCCCS) installed at the E.W. Brown coal-fired electric generating plant in Harrodsburg, Kentucky. The modification included installation of a water wash scrubber system on the CO_2 absorber tower with an activated carbon bed system to remove accumulated organic compounds in the water wash solution. The objective was to evaluate the performance of the additional air emission control equipment and determine any affect upon previously identified environmental, health or safety concerns. The evaluation was based upon test results obtained in August and September 2019. The objective also included evaluation of potential impact upon environmental permitting of a larger scale (500 MWe) PCCCS.

5.1 Toxicity Health Risk Summary

The PCCCS uses a proprietary amine based solvent to remove CO_2 from the flue gas stream. Toxicity associated with amine solvents is chemical irritation following direct contact. They are not classified as carcinogens and show little, if any, ecotoxicity. Due to possible irritation and other hazards, direct exposure to CO_2 capture solvents should be avoided and appropriate PPE used when handling these materials.

Ammonia was detected in all of the samples collected during the test run. The industrial inhalation RSL for ammonia is 2,200 ug/m^3 based on a noncancer health risk. All of the sample concentrations of ammonia (average for absorber exit = 13,550 ug/m^3; average for water wash exit = 11,700 ug/m^3) exceed the RSL for a full-time industrial worker exposure scenario. Exceedance of the RSL indicates a potential health risk that will need to be managed with appropriate PPE.

In addition, formation of nitrosamines may occur from the degradation of amine solvents used during the CO_2 capture process. Nitrosamine analysis was conducted on a limited number of samples (August 14, 2019) with no nitrosamine compounds detected. Improved sample and analysis techniques yielded levels of detection (LoD) generally an order of magnitude lower than the prior campaign in 2015; however, even one half of the lower levels of detection are still at least ten times greater, and in some instances, orders of magnitude greater than the respective EPA RSLs for a full industrial inhalation exposure scenario. Exposures to process gases should be avoided and process design should consider additional emission control, especially when applied to larger scale pilot facilities. The results do indicate, that the relatively low run time of the test run, and the actual sampling time would not result in significant levels of exposure to possible nitrosamines.

5.2 Air Emissions

Given the narrow scope of the EH&S evaluation, comparison of the 2019 sample results with results provided in a prior report (SMG, 2017) was not necessary to evaluate the performance and associated environmental impacts of the add-on water wash system for the primary absorber. Instead, evaluation of pollutant gas measurements upstream and downstream of added water wash system was the focus of this EH&S evaluation. **Appendix A** results demonstrate substantial reduction in amine emissions (94.5% for average detected ppmV results) and a moderate reduction in amine solvent degradation product ammonia emission (13.7% average) from the absorber. No additional control or change in air emissions was identified for the solvent stripper columns.

Actual air emissions from the operation of the 0.7 MWe PCCCS (since the 2017 EH&S report) do not present an unacceptable or insurmountable environmental risk

While the reduction in amine emissions is impressive, the observed emission reductions do not change permitting requirements summarized in the prior EH&S report (SMG, 2017). Source classification for air permits (550 MWe PCCCS) or exemptions (0.7 MWe PCCCS) remain appropriate.

A 550 MWe PCCCS located at an existing coal-fired steam electric plant would be subject to federal review under EPA's NSR permitting program, trigger PSD requirements to install BACT, and could also require EPA's most stringent control technology standard LAER for any CAP subject to NA-NSR permit requirements. BACT or LAER control measures for RAP emissions can add significant costs to the installation and operation of a 550 MWe PCCCS.

The permitting procedure for a source subject to NSR permit requirements (PSD and/or NA-NSR) will require a minimum of 1.5 – 2.5 years for regulatory preconstruction approval. Nothing identified in this EH&S assessment changes previous conclusions (SMG, 2017) about the significant air permitting requirements anticipated for installation and operation of a 550 MWe PCCCS.

5.3 Water/Wastewater Management

No additional land disturbance was required for this evaluation. Findings and conclusions from the prior assessment have not changed. Due to its relatively small footprint and location on an existing industrial site, the pilot project did not require a construction permit for storm water discharges. Depending upon the location, a larger scale facility will likely require a permit and storm water pollution plan implemented prior to construction.

There was no substantial change in wastewater characteristics or volumes due to the addition of the additional air emission control system on the absorber.

5.4 Waste Management

A waste determination is required for each solid waste generated as part of the project. All solid wastes were disposed off site in strict accordance with RCRA requirements. The only new waste generated from the system is spent activated carbon used to polish the water wash system. Evaluation of hazardous waste characteristics will need to include testing for toxic metals, including selenium, arsenic and mercury.

As reported previously, most wastes were not characterized as a hazardous waste and were approved for disposal off site. No RCRA F, K, P, or U listed wastes were generated and no ignitable, corrosive or reactive hazardous wastes were generated. Spent H3-1 solvent was characterized as a toxic hazardous waste due to selenium concentrations. This is not unusual for coal fired flue gas CO_2 absorber solvents. More frequent solvent reclamation may reduce the amount of selenium characteristic hazardous wastes generated, but it is unlikely they can be totally eliminated.

The types of wastes generated are not unusual for a large industrial facility, and do not represent a uniquely hazardous concern when managed properly. The amount of waste generated by a larger scale facility will increase with the size of the facility, but likely economies of scale should enable the increase to be less than directly proportional to the size increase.

5.5 Employee Hazards

This project did not use any new materials or materials with different hazard characteristics than evaluated in the prior assessment. The primary health hazards from raw material handling were derived from the amine CO_2 scrubbing solvent identified as corrosive and an irritant. The solvent is mixed with water, which reduces the hazard, but use of appropriate PPE by employees was required to minimize these hazards. The remaining raw materials did not represent substantial health concerns, when appropriate precautions were used to avoid accidents and injuries. Safety hazards included potential exposure to noise, heat, steam and pressure vessels, but these are not unusual for an industrial facility and can be managed with appropriate precautions to avoid accidents and injuries.

As noted previously, potential inhalation exposures to nitrosamines during operation of the facility may exceed USEPA acceptable risk ranges. However, the relatively low run time of this pilot system test campaign and the actual sampling time would not result in significant levels of exposure to possible nitrosamines.

Evaluation of detectable nitrosamine compounds in any carbon polishing waste, recirculated amine solvent and reboiler sludge is also recommended to determine potential human hazards from exposure to waste management and identify any new protective measures to be deployed.

5.6 Community Impacts

The addition of air emission controls on the absorber did not add substantially to the PCCCS footprint. No change in the prior assessment's evaluation, which identified no significant adverse community impacts from operation of the proposed pilot plant.

The added control reduced amine emissions from the absorber and would likely have reduced any potential nitrosamine emissions. No nitrosamine compound was detected at the improved LoDs; however, if nitrosamines were present at half of the new LoDs, they would be 2-3 orders of magnitude higher than a generally recognized acceptable lifetime ambient air exposure value of 3 ng/m^3 developed by NIPH. Depending upon the stack height and local topography and meteorological conditions, air dispersion may reduce ground level exposures of the community to levels below this acceptable lifetime value. Recent literature indicates that photolysis can degrade or destroy nitrosamine compounds in the air over relatively short periods of time, which might suggest a higher “acceptable” air emission value at the exhaust stack with adequate air dispersion contributing to lower ground level concentrations and lower potential risk to the surrounding community.

Improvement in analytical testing techniques to reduce the LoD for nitrosamine compounds will need to be developed to accurately characterize potential health risks from employee or community exposure to potential nitrosamine compound generation. Actual values for emissions from any PCCCS would need to be quantified and ambient dispersion would need to be evaluated to accurately assess the risk of what a person on the ground would be exposed to over a lifetime.

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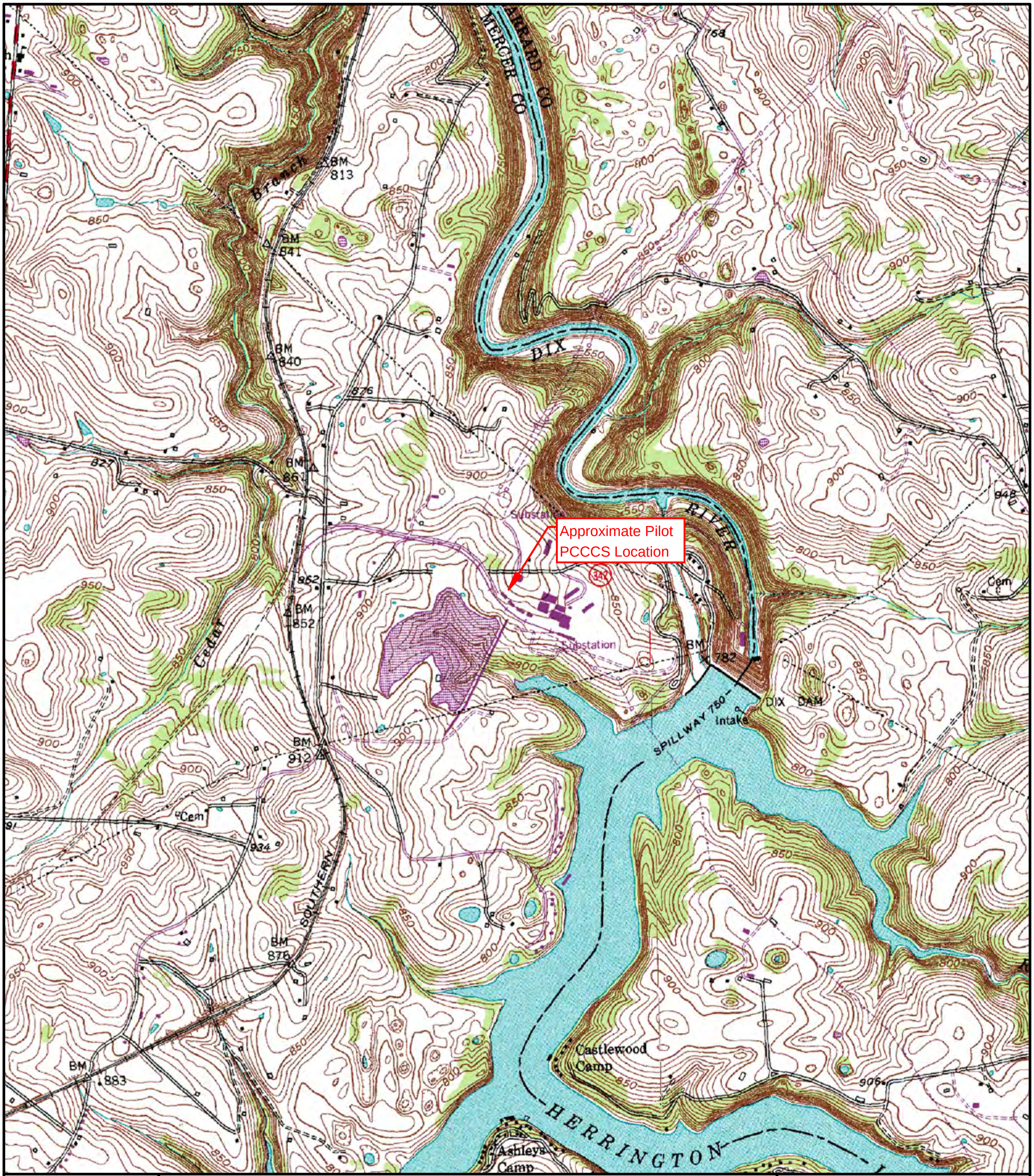
FIGURES



N

QUADRANGLE INFORMATION

WILMORE, KY - 1952
PHOTOREVISED - 1979

UK
UNIVERSITY OF
KENTUCKY

CAER
Center for Applied Energy Research

SMG
Smith Management Group
1405 Mercer Road
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1860 B Williamson Court
Louisville, KY 40223

www.smithmanage.com

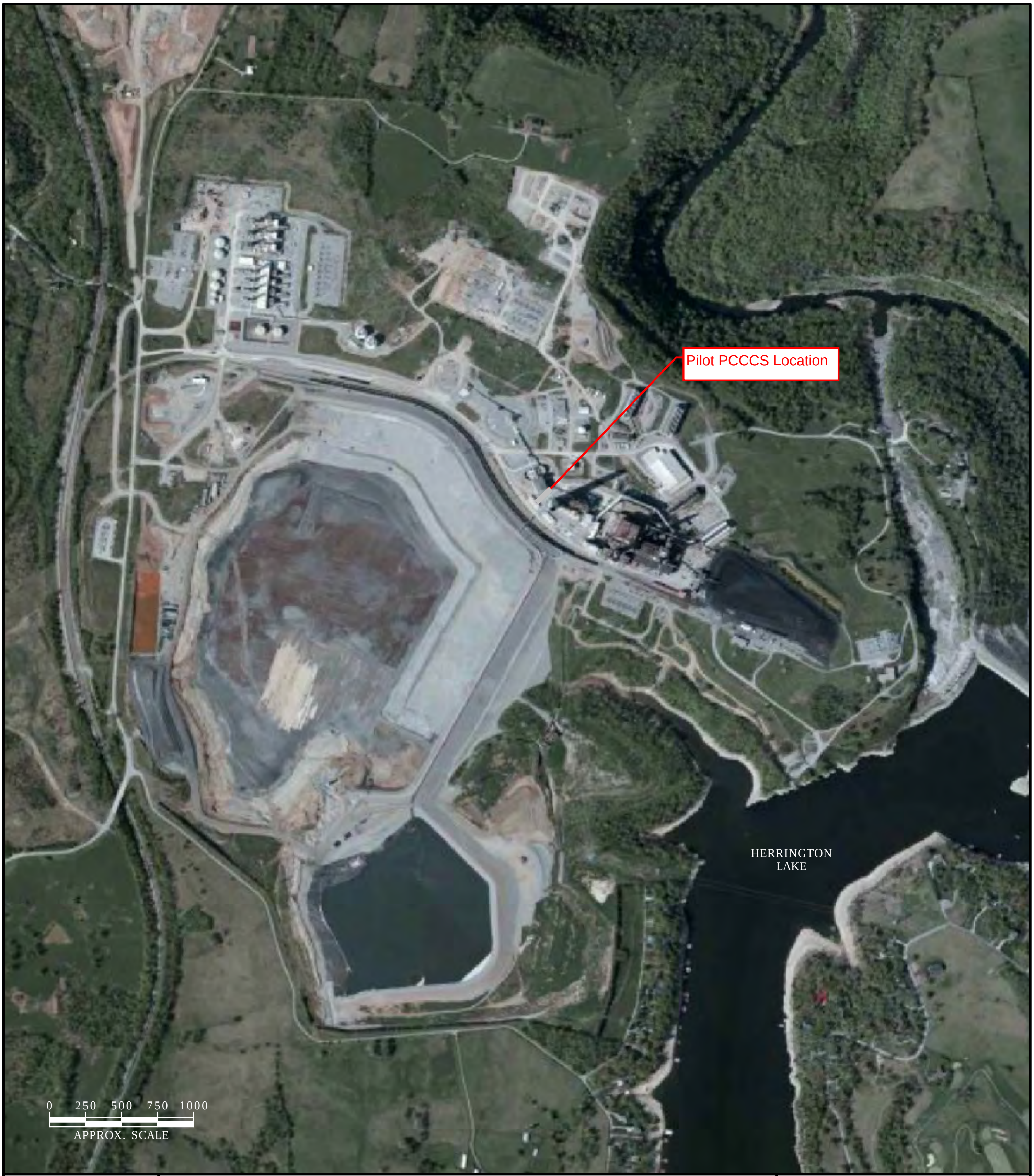
SITE LOCATION MAP

UK CAER PROPOSED CCS FACILITY
EW BROWN POWER PLANT
815 DIX DAM ROAD
HARRODSBURG, KENTUCKY

SCALE: 1"=2000'
DATE: 9/13/12
PREPARED BY: KAF
CHECKED BY: CTW

JOB NO.
2012-5267

FIGURE
1



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AERIAL SOURCE: FLASH EARTH

UNIVERSITY OF KENTUCKY

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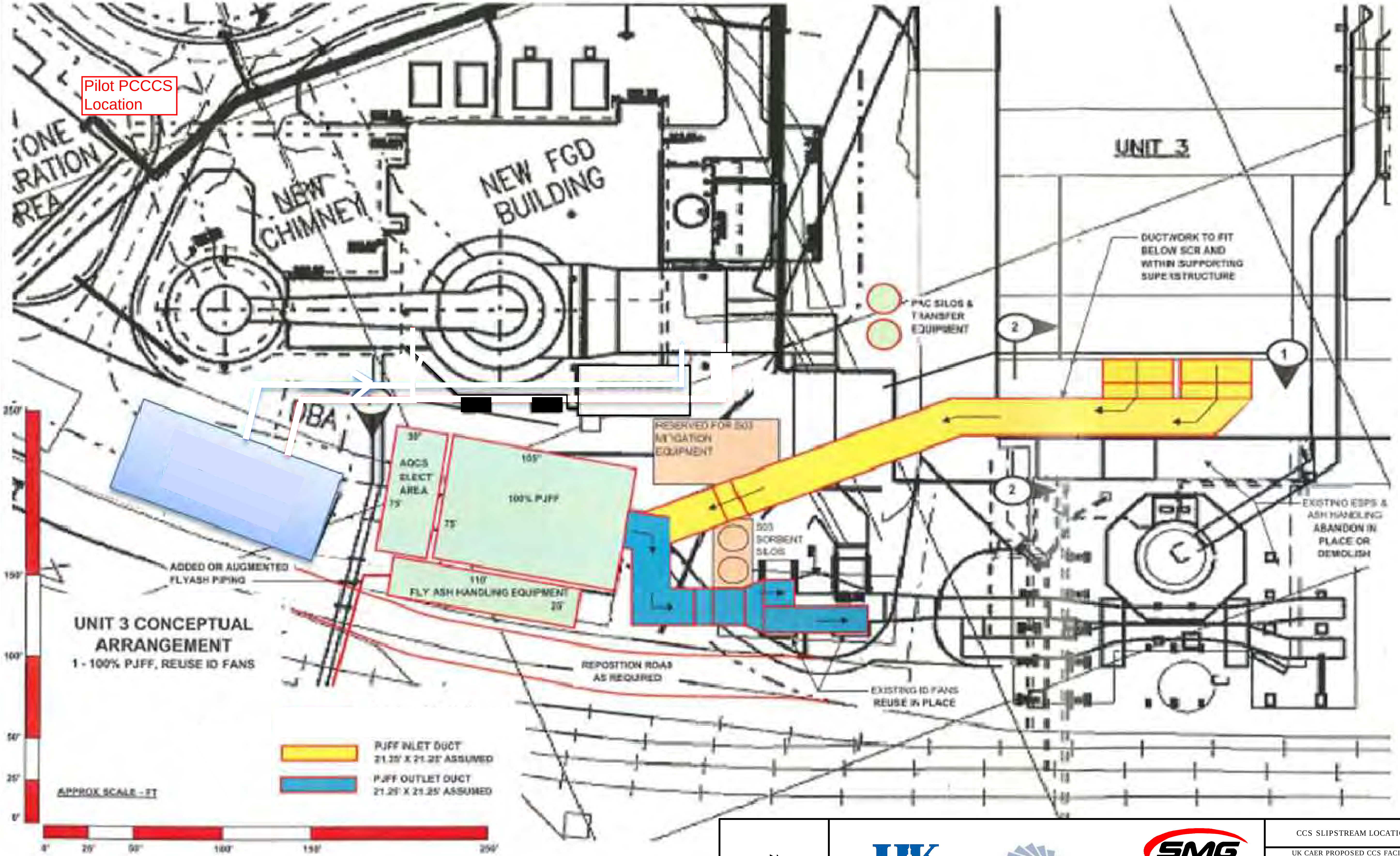
SITE VICINITY MAP

UK CAER PROPOSED CCS FACILITY
EW BROWN POWER PLANT
815 DIX DAM ROAD
HARRODSBURG, KENTUCKY

SCALE:	AS SHOWN	JOB NO. 2012-5267	FIGURE 2
DATE:	9/13/12		
PREPARED BY:	KAF		
CHECKED BY:	CTW		



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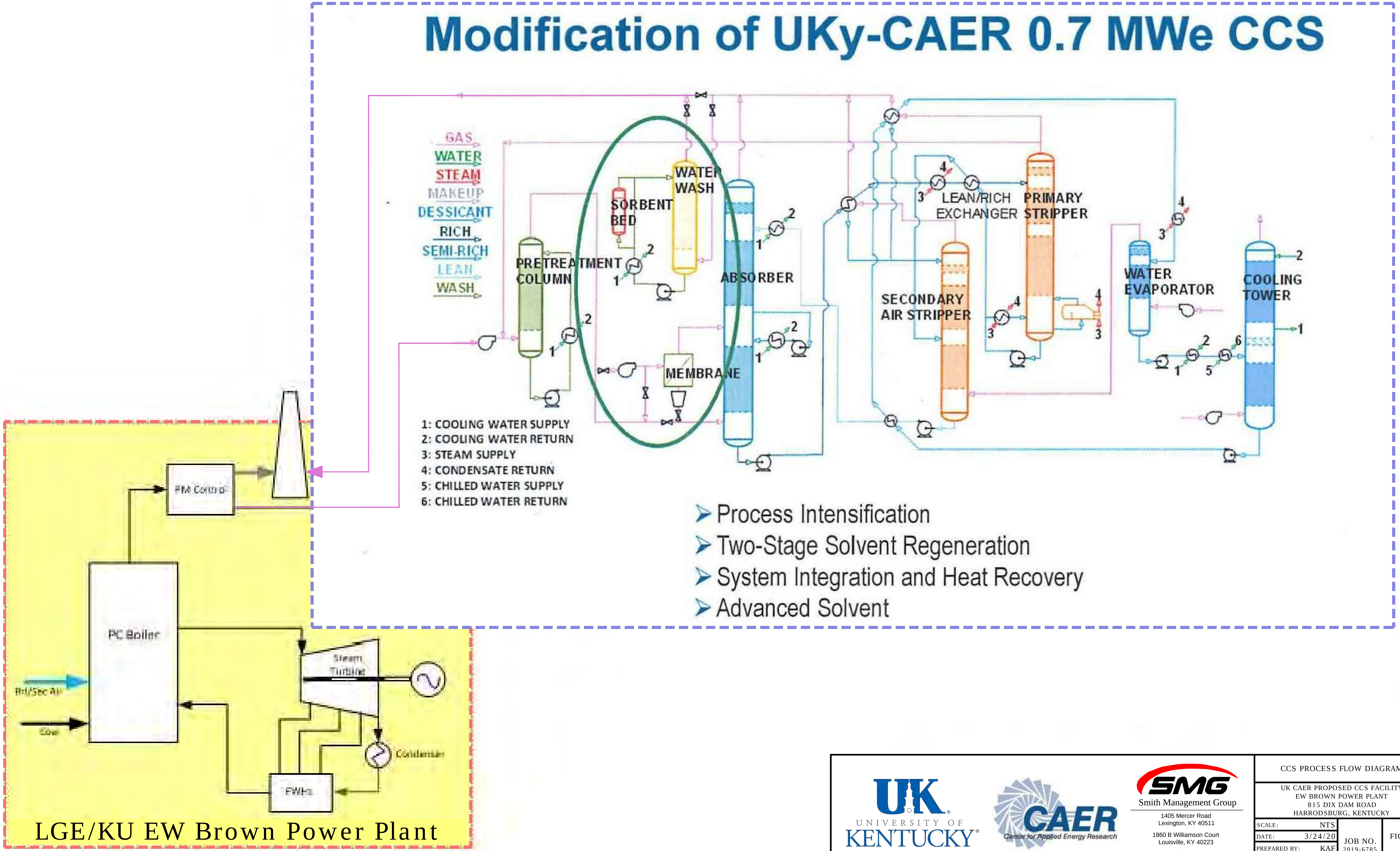
CCS SLIPSTREAM LOCATION

UK CAER PROPOSED CCS FACILITY
EW BROWN POWER PLANT
815 DIX DAM ROAD
HARRODSBURG, KENTUCKY

SCALE: AS SHOWN
DATE: 9/14/12
PREPARED BY: KAF
CHECKED BY: CTW
JOB NO. 2012-5267
FIGURE 3



Modification of UKy-CAER 0.7 MWe CCS

1: COOLING WATER SUPPLY
2: COOLING WATER RETURN
3: STEAM SUPPLY
4: CONDENSATE RETURN
5: CHILLED WATER SUPPLY
6: CHILLED WATER RETURN

- Process Intensification
- Two-Stage Solvent Regeneration
- System Integration and Heat Recovery
- Advanced Solvent

LGE/KU EW Brown Power Plant

UK UNIVERSITY OF KENTUCKY

CAER Center for Applied Energy Research

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CCS PROCESS FLOW DIAGRAM

UK CAER PROPOSED CCS FACILITY
EW BROWN POWER PLANT
815 DIX DAM ROAD
HARRODSBURG, KENTUCKY

SCALE:	NTS	JOB NO. 2019-6785	FIGURE 4
DATE:	3/24/20		
PREPARED BY:	KAF		
CHECKED BY:	CTW		

2019 EW Brown PCCCS Ammonia and Amine Test Results

Date	Sample Port	Ammonia (ppmV)	Ammonia (µg/m^3)	Amine (ppmV)	Amine (µg/m^3)
8/6/2019	Absorber Exit	19.46	13,750	20.06	117,300
8/6/2019	Absorber Exit	18.71	13,220	17.09	107,000
8/6/2019	Absorber Exit	18.39	12,990	18.96	119,000
8/7/2019	Absorber Exit	14.20	10,030	0.577	6.756
8/7/2019	Absorber Exit	16.10	11,380	5.11	3,312
8/8/2019	Absorber Exit	18.77	13,260	6.96	45,590
8/8/2019	Absorber Exit	19.80	13,980	8.38	52,940
8/8/2019	Absorber Exit	18.90	13,350	8.04	51,100
8/13/2019	Absorber Exit	14.32	10,120	4.63	34,220
8/13/2019	Absorber Exit	14.32	10,120	4.55	31,240
8/13/2019	Absorber Exit	13.83	9,772	4.21	29,070
8/15/2019	Absorber Exit	18.42	13,010	5.85	38,790
8/15/2019	Absorber Exit	18.72	13,220	6.75	43,540
8/15/2019	Absorber Exit	14.81	10,460	3.57	38,840
9/13/2019	Absorber Exit	33.85	23,910	28.79	175,800
9/13/2019	Absorber Exit	34.33	24,250	24.30	145,500
	Range	*14.20 - 34.33*	*9,772 - 24,250*	*0.577 - 28.79*	*6,757 - 175,800*
	Average	***19.18***	***13,550***	***10.49***	***64,578***

Date	Sample Port	Ammonia (ppmV)	Ammonia (µg/m^3)	Amine (ppmV)	Amine (µg/m^3)
8/6/2019	Water Wash Exit	10.51	7,423	*0.580*	*10,650*
8/6/2019	Water Wash Exit	13.28	9,380	*0.569*	*8,384*
8/6/2019	Water Wash Exit	9.75	6,888	*0.571*	*11,280*
8/7/2019	Water Wash Exit	8.89	6,281	*0.566*	*12,230*
8/7/2019	Water Wash Exit	9.70	6,855	*0.576*	*11,430*
8/8/2019	Water Wash Exit	12.54	8,855	*0.569*	*8,847*
8/8/2019	Water Wash Exit	17.30	12,220	*0.583*	*6,670*
8/8/2019	Water Wash Exit	14.99	10,590	*0.583*	*7,629*
8/13/2019	Water Wash Exit	16.52	11,670	*0.566*	*6,778*
8/13/2019	Water Wash Exit	14.73	10,400	*0.574*	*7,647*
8/13/2019	Water Wash Exit	12.96	9,152	*0.583*	*8,765*
8/15/2019	Water Wash Exit	15.00	10,600	*0.555*	*7,281*
8/15/2019	Water Wash Exit	16.18	11,430	*0.566*	*6,912*
8/15/2019	Water Wash Exit	19.83	14,010	*0.584*	*5,894*
9/13/2019	Water Wash Exit	37.76	26,670	*0.544*	*3,100*
9/13/2019	Water Wash Exit	34.95	24,690	*0.586*	*3,535*
	Range	*8.89 - 37.76*	*6,281 - 26,670*	*0.544 - 0.586*	*3,100.40 - 12,230.89*
	Average	***16.56***	***11,700***	***0.572***	***7,940***

2019 EW Brown PCCCS Nitrosamine Levels of Detection*

Date	Location	NPIP (ppmV)	NDMA (ppmV)	NMEA (ppmV)	NDEA (ppmV)	NDPA (ppmV)	NPY (ppmV)	NDBA (ppmV)
8/14/2019	Water Wash Exit	*0.00004667*	*0.00010420*	*0.00010950*	*0.00007980*	*0.00004258*	*0.00012917*	*0.00011840*
8/14/2019	Water Wash Exit	*0.00003554*	*0.00007932*	*0.00008342*	*0.00006078*	*0.00003242*	*0.00009837*	*0.00009017*
	Average	***0.00004111***	***0.00009176***	***0.00009646***	***0.00007029***	***0.00003750***	***0.00011377***	***0.00010429***

Date	Location	NPIP (µg/m^3)	NDMA (µg/m^3)	NMEA (µg/m^3)	NDEA (µg/m^3)	NDPA (µg/m^3)	NPY (µg/m^3)	NDBA (µg/m^3)
8/14/2019	Water Wash Exit	*0.2224*	*0.3210*	*0.4014*	*0.3391*	*0.2306*	*0.5380*	*0.7794*
8/14/2019	Water Wash Exit	*0.1694*	*0.2444*	*0.3057*	*0.2582*	*0.1756*	*0.4097*	*0.5936*
	Average	***0.1959***	***0.2827***	***0.3536***	***0.2986***	***0.2031***	***0.4738***	***0.6865***

* No nitrosamine compounds detected at the reported ppmV levels.