

CASE EXAMPLE

KRAFT PULP MILL EXPANSION PROJECT

This case example will illustrate the principles in developing specific permit conditions to account for specific regulatory requirements and to provide an enforceable set of permit conditions for the agency. Background information on the kraft process is provided in Appendix A for use in the evaluation of this permit example, if needed.

BACKGROUND INFORMATION ON PROPOSED MODIFICATION

The kraft pulp mill, located in an area designated as attainment or unclassifiable for all criteria pollutants, proposes to expand its production capacity by upgrading and fully utilizing current paper machine capacity and replacing an existing kraft recovery boiler (designated as Recovery Boiler No. 1) with a new, low-odor recovery boiler of a larger capacity (designated as Recovery Boiler No. 3). Paper making capacity was installed during a previous mill expansion but could not be fully utilized for a number of technical reasons. Sufficient steam capacity is available at the mill to operate at the higher production rate, although it has not been utilized due to the technical problems associated with the paper machine. The company provided documentation showing that it has been working to remove the technical limitations of the paper machine and expects to achieve the production levels allowed under a previous PSD permit. A 1000 ton/day recovery boiler (designated as Recovery Boiler No. 2) was installed under the previous PSD permit and subject to the NSPS Subpart BB is operated at the facility but is not otherwise involved in the mill expansion plans. The replacement of the existing recovery boiler would result in a substantial reduction of particulate matter due to the replacement of the existing electrostatic precipitator with a substantially larger and more efficient design. In addition, the new low-odor design would result in a substantial decrease in the generation of (TRS) compounds. The installation of the new recovery boiler to replace Recovery Boiler No.1 would result in a net decrease of TRS and particulate (PM_{10}) emissions. However, the new Recovery Boiler No. 3 would also result in a substantial increase in emissions of SO_2 and NO_x emissions. The new

Recovery Boiler No. 3 may, therefore, be considered a major source and be subject to the permit review requirements for PSD unless other emissions offsets are available. The old recovery boiler would not be dismantled as the company proposes to keep the boiler as an emergency standby boiler to be operated as an oil-fired boiler only in the event that one of the existing power boilers or either of the two recovery boilers is shutdown for maintenance.

There are several other sources located at the facility that will be involved in the plant expansion. There are currently four power boilers located on-site. Two of these power boilers burn solid fuel while the other two burn No. 6 fuel oil. One of the solid fuel-fired boilers burns woodwaste while the other is a coal/oil-fired boiler. In addition, two lime kilns are operated at the facility. One of the two kilns is subject to a previous PSD permit and NSPS limits under Subpart BB. Under the current equipment arrangement, TRS gases that are generated from the digestion of wood chips are vented to one of the two power boilers for incineration and destruction to form SO₂ (the other power boiler serves as the backup in the event the primary power boiler is shutdown). No controls are applied to the boilers for SO₂ control except regulatory limits on fuel sulfur content. The mill proposes to modify the equipment arrangement during the plant expansion. This change will include the rerouting of the NCG system from the digestion process from the power boilers to the lime kilns for destruction. The primary lime kiln designated for TRS incineration is the "existing", No. 1 Lime Kiln. The "new" No. 2 Lime Kiln, subject to the original PSD permit, will be designated as the back-up unit. The original configuration is shown in Figure 1 and the proposed changes are shown in Figure 2. The incineration of the TRS gases in the lime kiln instead of the power boilers will result in the TRS forming SO₂ in the kiln. However, it is anticipated that the presence of the lime in the kiln and in the existing scrubbers will capture SO₂. The combined effect of the SO₂ increase from the new recovery boiler and the SO₂ decrease from the power boilers from the change of the TRS incineration system will still result in a net increase in SO₂ emissions from the mill expansion project. However, the net increase was calculated to be below the significance levels for a major modification (40 TPY). As a result the State Agency determined that the modification is major for only NO_x and is subject to PSD review only for that pollutant.

The BACT analysis provided with the permit application indicated that NO_x would be limited through combustion air and excess air controls. Technological limitations prevented the use of additional external controls for the control of NO_x.

Increased production at the facility would result in an increase in wood and chip handling in the wood yard. Emissions increases from these areas include increased truck traffic as well as the actual handling of logs and wood chips. The increased emissions associated with the production increase were not considered during the previous PSD permit application and review. They are, however, being considered in this application.

Other On-site Processes

The other major emission producing processes located on the site include the four power boilers. These boilers each provide a portion of the steam and electrical requirements for the pulp mill. Two of the power boilers are oil-fired and do not have add-on controls. These boilers (designated Power Boilers 1 and 2) are not involved directly in the expansion although the full steam capacity of these boilers may be needed upon resolution of the technical problems associated with the paper machine operation. The other two boilers are a coal-fired boiler (designated as Power Boiler No.3) and a woodwaste-fired boiler (designated as Power Boiler No. 4). Emission controls for Power Boilers 3 and 4 are for particulate only. Emissions of SO₂ and NO_x are regulated to specific limits but no external controls are directly applied to reduce or control these pollutants from any of the power boilers.

The NCG system is currently vented to two of the power boilers for destruction of TRS gases from the various processes. Only one of the boilers is designated as the primary destruction device. The other boiler is reserved as a backup device in the event a boiler is shutdown while other processes producing NCG are operational. Normally, Power Boiler No. 3 is used for the destruction of TRS gases from the NCG system and is reflected in the emission summary tables provided. The use of the power boilers are also quite common for TRS control and NCG incineration. Care

must be taken to prevent the buildup of turpentine in the NCG system but the combustion system is not as sensitive to variations in gas flow as a lime kiln may be.

Another source of TRS containing NCG is a steam stripper used to strip TRS compounds from *foul condensates*. The steam stripper passes steam through foul condensates from sources such as the MEE condensate streams and removes the TRS compounds dissolved in the condensates. The NCG from the stripper are vented to the NCG system. One of the principle advantages to this system is the reduction of atmospheric TRS emissions from water treatment systems such as aerated treatment ponds. In addition, the reduction of the TRS content of the wastewater lowers the biological oxygen demand (BOD) of the water treatment system. Although the proposed modification does not explicitly include the steam stripper located at this facility, the increased production will result in increased processing of foul condensates.

Two lime slakers will be located in the causticizing area. The No. 2 Lime Slaker will provided added capacity and redundancy to the causticizing operation. Although the actual throughput through each slaker will be less than that specified in the permit application, the maximum production rate and hours of operation were used to estimate emission rates to avoid permit restrictions on hours of operation and/or production rate.

Emissions Summary

The facility provided an emission summary for each source based on actual operation and emissions from the previous two years with the exception of the two oil-fired power boilers which have been operated below design parameters due to the aforementioned paper machine problems. The values shown for the power boilers reflect the values that were originally allowed under the previous PSD permit and that are expected to be achieved upon completion of the mill expansion. These values are shown in Tables 1, 2, and 3 and were used as the basis for the applicability determination and the required BACT analysis. As mentioned previously, Figures 1 and 2 show the configuration of the system before and after the proposed changes.

**TABLE 1
ACTUAL EMISSIONS PRIOR TO PROPOSED MILL EXPANSION**

SOURCE	PRODUCTION RATE		STACK HEIGHT	STACK DIA., FT	GAS FLOW ACFM	TEMP F	VELOCITY FT/MIN	TSP(PM10)	EMISSIONS - TONS/YR				
	ADT/D	MMBTU/HR							SO2	NOx	VOC	TRS	CO
POWER BOILER 1	N/A	242	122	8.0	110000	320	2188	84	2514	447	5.1	-	33.4
POWER BOILER 2	N/A	248	208	7.0	111500	340	2897	86	2576	458	5.2	-	34.2
POWER BOILER 3	N/A	553	181	9.5	289150	410	4079	119	8713	1641	28	-	93
POWER BOILER 4	N/A	659	250	7.0	325000	350	4222	281	2309	842	646	-	646
RECOVERY BOILER 1	593	352	250	16.7	186000	240	849	466	977	253	150	63	1158
RB 1 SMELT TANK	593	N/A	129	4.0	21600	145	1719	11	21	-	-	2	-
RECOVERY BOILER 2	1253	743	287	9.0	368160	325	2894	306	1441	660	431	32	-
RB 2 SMELT TANK	1253	N/A	289	4.5	50500	150	1588	35	22	-	-	3	-
LIME KILN 1	1667	N/A	125	6.0	60700	165	2147	199	47	164	63	30	2164
LIME KILN 2	1467	N/A	150	4.8	36230	169	2045	126	30	96	37	7	-
SLAKER 1	3710	N/A	112	3.0	10650	200	1507	50	-	-	-	-	-
ACTUAL EMISSION TOTALS, TONS/YEAR								1763	18650	4561	1365	137	4129

**TABLE 2
ACTUAL EMISSIONS AFTER PROPOSED MILL EXPANSION**

SOURCE	PRODUCTION RATE		STACK HEIGHT	STACK DIA., FT	GAS FLOW ACFM	TEMP F	VELOCITY FT/MIN	TSP(PM10)	SO2	EMISSIONS - TONS/YR			
	ADT/D	MMBTU/HR								NOX	VOC	TRS	CO
POWER BOILER 1	N/A	242	122	8.0	110000	320	2188	84	2514	447	5.1	-	33.4
POWER BOILER 2	N/A	248	208	7.0	111500	340	2897	86	2576	458	5.2	-	34.2
POWER BOILER 3	N/A	553	181	9.5	289150	410	4079	119	8074	1641	28	-	93
POWER BOILER 4	N/A	659	250	7.0	325000	350	4222	281	2309	842	646	-	646
RECOVERY BOILER 1*		352	250	16.7	186000	240	849						
RECOVERY BOILER 2	1253	743	287	9.0	368160	325	2894	306	1441	660	431	32	-
RB 2 SMELT TANK	1253	N/A	289	4.5	50500	150	1588	35	22	-	-	3	-
RECOVERY BOILER 3	1000	748	290	10.0	360000	360	2292	266	1348	488	153	25	1017
RB 3 SMELT TANK	1000	N/A	290	5.0	50883	150	1296	36	36	-	-	4	-
LIME KILN 1	1667	N/A	125	6.0	60700	165	2147	199	300	164	63	30	2000
LIME KILN 2	1467	N/A	150	4.8	36230	169	2045	126	30	96	37	7	-
SLAKER 1	3710	N/A	112	3.0	10650	200	1507	50	-	-	-	-	-
SLAKER 2	3710	N/A	112	3.0	10650	200	1507	50	-	-	-	-	-
ACTUAL EMISSION TOTALS AFTER EXPANSION, TONS/YEA									18650	4796	1368	101	3824
ACTUAL EMISSIONS BEFORE EXPANSION, TONS/YEAR									18650	4561	1365	137	4129
NET CHANGE AFTER EXPANSION, TONS/YEAR									0	235	3	-36	-305

*RECOVERY BOILER 1 WILL BE USED AS A STANDBY OIL-FIRED BOILER TO REPLACE LOAD LOSS FROM POWER BOILERS 1 OR 2

**TABLE 3
NET EMISSIONS CHANGE FROM POINT SOURCES**

SOURCE	EMISSIONS - TONS/YR					
	TSP(PM10)	SO2	NOx	VOC	TRS	CO
POWER BOILER 1	-	-	-	-	-	-
POWER BOILER 2	-	-	-	-	-	-
POWER BOILER 3	-	-639	-	-	-	-
POWER BOILER 4	-	-	-	-	-	-
RECOVERY BOILER 1*	-466	-977	-253	-150	-63	-1158
RB 1 SMELT TANK	-11	-21	-	-	-2	-
RECOVERY BOILER 2	-	-	-	-	-	-
RB 2 SMELT TANK	-	-	-	-	-	-
RECOVERY BOILER 3	266	1348	488	153	25	1017
RB 3 SMELT TANK	36	36	-	-	4	-
LIME KILN 1	-	253	-	-	-	-164
LIME KILN 2	-	-	-	-	-	-
SLAKER 1	-	-	-	-	-	-
SLAKER 2	50	-	-	-	-	-
NET CHANGE, TONS/YEAR	-125	0	235	3	-36	-305

*RECOVERY BOILER 1 WILL BE USED AS A STANDBY OIL-FIRED BOILER TO REPLACE LOAD LOSS FROM POWER BOILERS 1 OR 2

PERMIT DRAFTING EXERCISE

The purpose of this exercise is for your team to draft permit conditions for one or more emission sources, as appropriate, at this facility to reflect the regulatory requirements and conditions presented in the permit application. Please answer Questions 1 through 5 below. After a brief discussion period your group will be asked to develop permit conditions for one or more assigned emission sources.

- 1. The permit to be written will be a PSD permit since the applicability determination found that the emission increases were significant for the pollutant NO_x. List the source or sources that should be included as part of this permit.

	<u>Source</u>	<u>Point or Fugitive</u>
a)	_____	_____
b)	_____	_____
c)	_____	_____
d)	_____	_____
e)	_____	_____
f)	_____	_____
g)	_____	_____
h)	_____	_____

- 2. Explain your reason(s) for selecting the source(s) listed in your answer to Question 1. _____

3. Examine the emission rate data in Tables 1, 2, and 3 for the proposed modifications and reductions in emissions of SO₂. With the information provided on the kraft process information (Appendix A) and the table, are there any technical concerns associated with the proposed modifications and if so how should they be addressed in the permit conditions?

4. The addition of the new recovery boiler (Recovery Boiler 3) will be subject to NSPS Subpart BB as a minimum requirement under PSD. The applicability determination indicated that this was the only source that would be subject to the review requirements under PSD for NO_x. Are there any other sources that you would identify that may be subject to NSPS requirements as a result of the proposed modification? Identify these sources, if any, below.

APPENDIX A

BACKGROUND INFORMATION ON PROCESSES AT A KRAFT PULP MILL

The kraft pulping process is a chemical process designed to manufacture paper and paper products from woodchips. This section provides a brief summary of the kraft pulping process to aid in your evaluation of the proposed modification. Other, more detailed, technical resources are available on the pulping process as are regulatory requirements. Additional technical and regulatory information will be provided to you, as needed, to complete this exercise.

The kraft pulping process utilizes a chemical dissolving process to *digest* wood chips and produce the cellulose required for paper manufacturing. Many of the operations at a pulp mill are associated with the separation of the chemicals from the pulp and the recovery of these chemicals. The paper products produced may be bleached (white) or unbleached depending upon the equipment used at the facility and the market demands for the paper products.

Wood may be received at a pulp mill in several forms. It may be received in the form of logs by truck, rail, and if available, by barge. Wood received in log form must be debarked and chipped. The bark and undersized wood chips are usually used as a fuel supply for a woodwaste-fired boiler on site that provides a portion of the steam and electricity requirements for the paper mill. Wood may also be received as chips from other locations by truck, rail or barge. Wood, wood chips, and bark fuel are stored on outdoor storage piles until needed in the process.

Wood chips may be digested by either a continuous process or by a batch process. In the Eastern United States most pulp is manufactured using the batch process and the facility discussed in this example is using a batch process. Wood chips and cooking chemicals are placed in batch digesters in predetermined proportions and cooked under temperature and pressure to produce the pulp used in the paper manufacturing process. The cooking chemicals are a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) known as *white liquor*. During the cooking process, the binding material in the wood, known as *lignin*, is chemically dissolved into the cooking liquor in a complex reaction with the sodium hydroxide to release the cellulose fiber in the wood. The sodium sulfide acts as a buffer in the reaction and supplies a source of sodium in the complex reactions between the lignin

and the hydroxyl ion of the sodium hydroxide. During the reaction between the organic lignin molecules and the hydroxyl ion certain other reactions occur between the sulfide ions and the organic molecules to form *reduced sulfur* compounds. These compounds, known collectively as *Total Reduced Sulfur (TRS)* compounds, consist of molecules including hydrogen sulfide (H_2S), methyl mercaptan, dimethyl sulfide, and dimethyl disulfide and give the kraft pulping operations its characteristic odor.

During the digestion process, these TRS gases must be vented (*digester relief*). In addition, other compounds such as *terpenes* (the basis for crude turpentine) are also formed and must be vented. Eastern softwoods produce much more turpentine than either hardwoods or western softwoods and it is usually recovered by eastern pulp mills for further refining. The digester relief gases are passed through condensers to capture the crude turpentine and some of the TRS compounds. The remaining gases are considered *noncondensable gases (NCG)* and are usually vented to a boiler, lime kiln, or separate incinerator for incineration of the NCG. This collection and ventilation system is usually known as the *NCG system*.

At the completion of the cooking process the cellulose and spent chemicals (*black liquor*) are *blown*, under pressure, into a blow tank. The sudden release of pressure causes steam to flash from the liquor. The cellulose pulp is recovered from the blow tank along with the black liquor. The flashed steam is vented to a condensing system to recover the heat for use as hot water. The NCG released by the blowing operation are collected and vented into the NCG system.

The pulp is collected from the blow tanks and stored in tanks for washing. The pulp is washed to remove the black liquor from the pulp in *brown stock washers*. The black liquor is recovered and stored for further treatment. The washed pulp may then be bleached if needed for product specification. The pulp is resuspended in water and fed to the paper machine. The pulp is continuously fed to paper machine where it form a mat on a screen (*fourdrinier wire*) and is pressed and dried to form a continuous sheet on the paper machine. At the end of the paper machine the paper is rolled into large rolls which may then be processed further within the facility or shipped off-site for further processing.

The black liquor from the brown stock washers contains a mixture of spent chemicals (as complex organic compounds from the reaction of the white liquor with the lignin) and water. These dissolved materials, *black liquor solids*, are relatively dilute at this phase (approximately 10-13 percent by weight) and must be concentrated to allow for the recovery of the cooking chemicals. Concentration of the black liquor is usually accomplished by use of *Multiple Effect Evaporators (MEEs)* to reduce the quantity of water present and to increase the solids content. The MEEs are usually vented to the NCG system to control TRS emissions. The black liquor solids content is typically 47-48 percent solids after passing through the MEEs. Additional concentration of the black liquor is dependent upon the recovery boiler design.

Recovery Boiler

The recovery boiler is a combustion device designed to burn black liquor solids to produce steam and electricity for the paper mill while recovering the inorganic chemicals used in the kraft pulping process. The black liquor solids content must be raised to a minimum of 55-57 percent for stable combustion characteristics. The method used to raise the solids content above this minimum threshold depends upon the age and design of the recovery boiler.

Older, existing recovery boilers may use *direct contact evaporators* to increase the solids content. This is accomplished by contacting the black liquor that has been passed through the MEEs with the combustion flue gas from the recovery to utilize the available heat to raise the solids content. However, contact between the flue gas and the black liquor has the potential to react CO₂ and water with sulfide compounds in the black liquor to form TRS compounds, most notably H₂S. To limit the reaction to form H₂S compounds, black liquor is often oxidized to form thiosulfate compounds in the black liquor that will not react with flue gas components to form TRS compounds. The black liquor leaving the direct contact evaporator unit is often circulated through the electrostatic precipitator, used to capture particulate emissions from the recovery boiler, to return the inorganic chemicals to the recovery process. The particulate generated by the recovery boiler is sodium sulfate (Na₂SO₄, or *salt cake*). The black

liquor is then sent to the *guns* at a solids content of between 60 and 63 percent for combustion in the recovery boiler.

The recovery boiler operates with three distinct zones. The drying zone, the reducing zone, and an oxidizing zone. The black liquor is introduced to the recovery boiler through a set of guns that spray the black liquor into droplets in the drying zone. The droplets dry through contact with the flue gases and radiant energy in the furnace and ignite the organic compounds contained in the black liquor solids. The larger droplets fall to the bottom of the furnace which is maintained at an oxygen deficient, or reducing conditions. This reducing zone of the furnace accumulates *char* which, as the carbon is converted in the char bed, forms a liquid *smelt* that is drain from the bottom of the furnace. The smelt is a mixture of sodium sulfide and sodium carbonate (Na_2CO_3) which is dissolved in water to form *green liquor*, an intermediate recovery product from the recovery boiler. Finer particles are carried out of the reducing and drying zones of the recovery boiler and into the oxidizing zone. In this zone, combustion is completed with sufficient excess air to convert all sodium salts from the burning black liquor into salt cake. An electrostatic precipitator is the method used to control particulate emissions. As mentioned previously, the salt cake is recycled into the black liquor being sent to the guns.

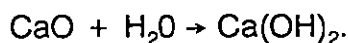
In addition to the TRS emitted from a direct contact evaporator, TRS emissions may be generated by the operating characteristics and design of the recovery boiler. Control of air flowing to the various zones within the furnace have a strong affect on the generation of TRS, SO_2 , and NO_x from the recovery boiler.

Low-odor recovery boilers have a substantially different design than the traditional recovery boiler equipped with a direct contact evaporator as described above. No direct contact between the black liquor and the recovery boiler flue gases occurs in this design. The black liquor solids content is increased by using a concentrator (essentially a specialized set of MEEs) to raise the solids content up to values approaching 70 percent solids. Salt cake from the electrostatic precipitator is added to the concentrated black liquor to recycle the sodium compounds back to the recovery boiler in a similar method to that employed for the direct contact design. Black liquor is also fired in a similar method to the direct contact design. The recovery

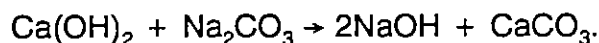
boiler design, however, allows for greater control of the air flow into the boiler and this improved level of control for TRS compounds. Smelt is drained from the low-odor recovery boiler in a manner similar to the direct contact design and dissolved to form green liquor.

Lime Kilns

The recovery of the cooking chemicals to form white liquor is accomplished by causticizing the green liquor. This is accomplished by reacting slaked lime with green liquor. Lime (calcium oxide) is mixed with water to form slaked lime following the reaction:



The reaction between the slaked lime and the green liquor is a simple ion exchange. The reaction between the sodium carbonate and calcium hydroxide follows the reaction:



The calcium carbonate (CaCO_3) forms an insoluble mud which is allowed to settle and is separated from the recausticized white liquor. The white liquor is then recycle back for use in digesting wood chips. The lime mud is washed, dewatered, and fed to a lime kiln to recalcine the carbonate to a usable lime. This calcining step breaks down the carbonate following the reaction:



with the addition of sufficient heat to the lime kiln. Care must be taken to adequately wash the lime mud and remove as much residual Na_2S as possible from the recausticizing step because this sulfide will be carried into the lime kiln and will react with the kiln flue gases to form H_2S when in contact with the CO_2 and water in the flue gas.

Not all of the lime mud will be converted back to lime for use in the causticizing step. A small portion will remain unreacted upon exiting the kiln. In addition, a portion of the lime will react with SO_2 formed from the combustion of kiln fuel or from the combustion of NCG in the combustion zone of the kiln to form calcium sulfate (CaSO_4). This sulfate forms a dead load in the kiln, which must be separated from the lime recycle loop. The sulfate is not soluble and is separated from the lime when the lime is slaked in water. It should be noted that the amount of SO_2 that is reacted to form CaSO_4 is related to a number of factors including kiln flame characteristics, excess air, and the kiln temperature profile.

Lime kilns are one of several pieces of process equipment that may be used to incinerate NCG to control odors from the wood digestion process. One of the advantages to the use of a lime kiln is its high operating temperature and destruction potential for TRS compounds. A principle disadvantage is the need for sophisticated flame control systems and the requirement for adequate removal of turpentine by the condensing system. Equalization of gas flow may be necessary to prevent large variation in NCG volumes and the possibility of kiln flameouts.