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Removal of Sulfur Dioxide from Boiler Scrubber Water

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Factory Description/History

The Mini-Cassia factory of the Amalgamated Sugar Company has a maximum slice capacity of 16,550 tons per day and maximum sugar production of 30,000 cwt. per day. The factory utilizes coal as the major energy source since the construction of the factory in the early 1900's. Several boiler changes have taken place since the early years resulting in the operation of the factory presently with two boilers for the above plant capacity. One is a stoker grate boiler rated at 175,000 lbs/hr and the other a pulverized coal boiler rated at 200,000 lbs/hr. The pulp dryers consist of two pulverized coal rotary drum type dryers (12' and 10.5' diameter).

The coal used for these boilers and dryers comes from the Kemmerer mine in Wyoming, and is classified as a Powder River Basin Coal. The sulfur content averages around 0.9% and the ash content averages 4%. This coal has been used for the last fifteen years almost exclusively at this plant. Natural gas is used on the pulverized boiler only for pilots and during repairs of the coal handling equipment.

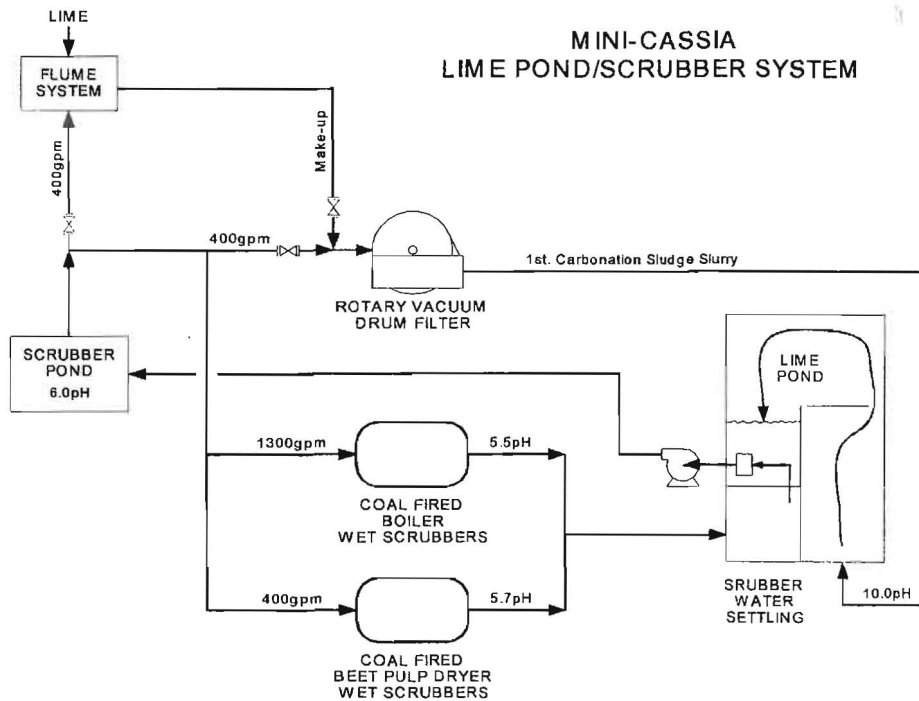
The Clean Air Act of the early seventies required cleaning of the flue gas emissions from these boilers. The pulverized boiler being installed in 1972 required pollution equipment to reduce emissions from the stack. The equipment installed consisted of two low pressure differential horizontal spray chamber type scrubbers, one for each boiler. These scrubbers were installed to remove particulates by utilizing water sprayed into the hot gases of combustion exiting from the boilers. In addition to the boilers, the pulp dryers also use coal for combustion, and the flue gas exiting the dryers is scrubbed with impingement type scrubbers.

The water exiting the scrubbers contains absorbed sulfur dioxide SO₂ from the combustion of sulfur in the coal. This scrubber water was then pumped to the lime pond to settle out the "scrubbed" particulates. Neutralization of the SO₂ was accomplished in the lime pond. The slurry water that transported the 1st Carbonation sludge from the clarifier underflow filters was combined in the lime pond with the scrubber water from the boilers and pulp dryers.

Although this system provided for "almost free" neutralization of the SO₂ by utilizing the basic pH of the 1st Carbonation sludge, the "neutralized" scrubber water caused severe scaling that had to be dealt with on a continual basis. The

scale was a combination of Calcium Sulfate and Calcium Sulfite. This scale was extremely tenacious and hard. Injecting anti-scaling chemicals and high pressure cleaning of pipes and equipment was routine. Redundant piping was installed to provide for operation while the other system was being descaled.

The lime pond/scrubber water entering back into the process was typically between 5.5 and 6.0 pH. At this pH, the SO₂ absorption efficiency across the scrubbers was around 80%. The pH of the scrubber water exiting the scrubbers typically dropped to around 5.0 to 5.5 pH (a 0.5 pH reduction). See Figure 1 for the basic flow sheet for this system.



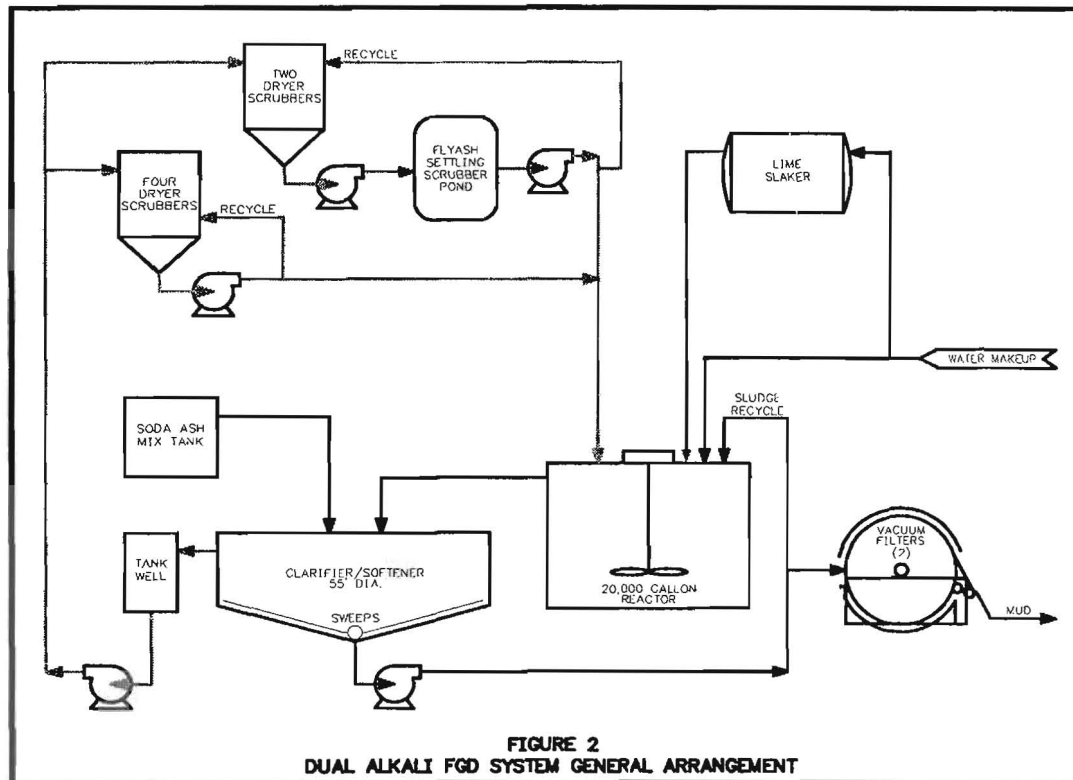
According to a mutually agreed upon environmental consent order with the Idaho Department of Environmental Quality, the lime pond is scheduled to be replaced by September of 2007. Since the lime pond operation has been the mechanism for scrubber water neutralization, a new system for scrubber water treatment was mandated to be installed and operational by September of 2005.

Due to the EPA Prevention of Significant Deterioration (PSD) regulations, the (SO₂) emissions had to remain the same or lower. Several options were considered and, as always, each had their advantages and disadvantages. The option chosen at the Mini-Cassia factory was the Dual Alkali Flue Gas Desulphurization System (FGD). Other typical systems would have required modification of the existing scrubbers due to chemistry and substantially different

scrubber water flow rate requirements. In addition, the system could have no negative impacts on the factory wastewater land application system.

Dual Alkali Flue Gas Desulphurization Process Description

An example of a dual alkali FGD system was visited and is currently in operation at a power plant located in Indiana where the SO₂ was removed in the form of a Calcium Sulfitite (CaSO₃) cake and hauled to an onsite land disposal area. This type of FGD was the option chosen to use at the Mini-Cassia plant. This system is self contained with no net hydraulic wastewater generation quantities. Since the Mini-Cassia factory is located in a semi-arid climate, the ending water in this system will be evaporated over the summer in a lined pond. As a result, there will be no impact on the wastewater land application system. See Figure 2 for the FGD basic flow sheet.

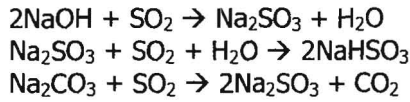


The goal of the Dual Alkali FGD system is to provide neutralization of SO₂, scale free operation, precipitation and filtration of key reactants. The two alkalis used in this process are lime and soda ash. The basic chemistry is as follows:

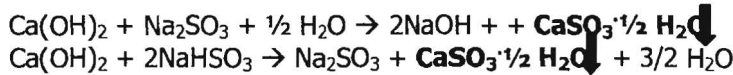
Scrubbing Liquor into the wet scrubber consists of soluble alkali (NaOH, Na₂SO₃, Na₂CO₃, NaHCO₃) which are used to neutralize the absorbed SO₂ from

the flue gas scrubbing process. The scrubber effluent is then reacted with lime (Ca(OH)₂) to precipitate the insoluble CaSO₃·½H₂O and CaSO₄·2H₂O and regenerate the sodium based soluble alkali for recycle back into the wet scrubber.

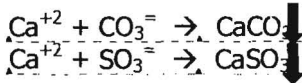
Absorption Reactions (Flue Gas Wet Scrubber Treatment Reactions):



Regeneration Reactions (Lime Reactor Reactions):



Softening Reactions



An essential aspect of the system is to operate with little or no scale in the scrubbers. This is achieved by adding make-up sodium to the system as sodium carbonate and by maintaining a significant concentration of sodium sulfite in the regenerated liquor. Since calcium sulfite and calcium carbonate are very insoluble compared to calcium sulfate, the presence of sulfites and carbonates in the regenerated liquor lowers the concentration of soluble calcium in the liquor going back to the scrubbers. The result is that the driving force for precipitation of gypsum scale in the scrubbers is virtually eliminated.

This Dual Alkali FGD process is only successful if the oxidation rate of the sulfite in the system is minimized. If the oxidation rate is too high, the sulfite chemistry cannot be maintained, resulting in buildup of both calcium and sulfate in the process liquor, which lead to scaling in the scrubbers.

Mini-Cassia Dual Alkali Installation

There were two big differences between the Mini-Cassia factory and the Indiana power plant: 1- the power plant removed the fly ash in the flue gas before it entered into the FGD system and 2- the power plant did not have a pulp dryer to treat in the scrubber water system. Both of these differences played a significant role in the FGD system at Mini-Cassia.

The flow schematic, shown in figure 2, indicates the basic equipment required to operate the FGD system. The system design was under the direction of Jim Wilhelm of Codan Associates of Sandy, Utah. Jim has over 30 years of experience with dual alkali scrubbing processes and has helped design many

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combustion gas treatment systems throughout the United States. Jim's knowledge and experience was used extensively in the development of the FGD system at Mini-Cassia. Installation of the new system began in early 2004 and was put in service in September 2004. The capital cost for this system amounted to \$2,564,000. The automated installation resulted in no increase in factory labor. Initial operation began on the boilers during the 2004 juice run which was just previous to the 2004 beet campaign.

Dual Alkali FGD Operation Results

After the boiler FGD chemistry was at steady state, the pulp dryer scrubber water was incorporated into the operating FGD system. Within two hours, the dryer had to be removed from the system due to upset of the FGD chemistry resulting in high scrubber liquor hardness and severe scaling. The conditions across the dryer scrubbers resulted in high oxidation rates producing unacceptable levels of sulfate. Without significant concentrations of sulfite and with increasing sulfate concentration, the hardness levels increased, resulting in gypsum scaling. The dryer had to be taken out of the FGD treatment loop and alternate methods of operation had to be developed to allow the dryer to be incorporated into the FGD system.

As part of the chemistry to maintain the proper pH in the scrubber, a portion of the scrubbing liquor exiting the scrubbers was immediately recycled into the scrubber inlet. This mode of operation presented a serious problem of severe erosion. The scrubbed fly ash became an aggressive grinding compound and wore through almost anything that it came into contact with. While this was an initial design concern, the extent of the erosion was significantly higher than expected. The fly ash eroded the nozzles so rapidly, that it became very difficult to stay ahead of replacement verses wear. In addition, the fly ash abraded strainer screens, pumps and piping with no abatement in sight.

In an effort to reduce the scrubber spray nozzle abrasion, recycle of the flash laden scrubber water effluent was halted. The main disadvantage of this option was that the pH of the lime reactor and clarifier had to be lowered from the 10 pH range down to the 7 pH range. The operation at 7 pH produced a sludge that had poor settling and filtration characteristics. As a result, the FGD system was temporarily shut down.

As a remedy to the abrasion issue, the scrubber water effluent system was modified. The scrubber water exiting the scrubbers, which includes the entrained fly ash, is pumped to a hypalon lined holding pond to allow the fly ash to settle out. The "fly ash" clarified scrubber liquor is then returned as recycle back into the FGD system. This has proven to be successful and the wear has been all but eliminated. The fly ash settled in this pond is periodically dredged and combined with the FGD solids along with boiler ash. The FGD solids that are

filtered out by the rotary vacuum drum filters are hauled, mixed with ash, and stockpiled on top of the old abandoned lime pond.

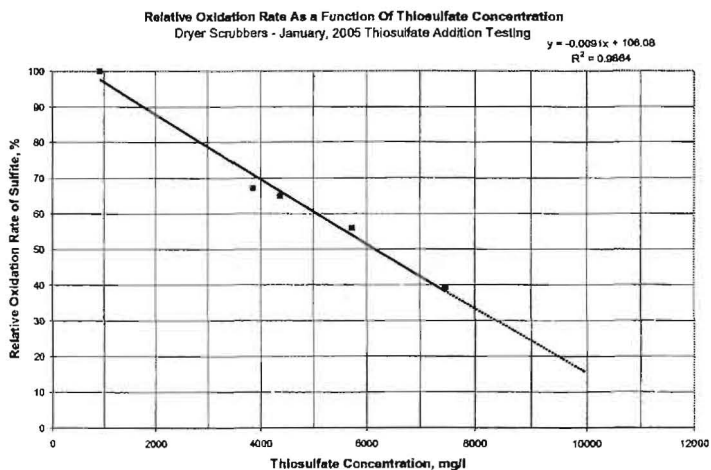
Recent preliminary stack testing results have shown that the SO₂ absorption efficiency is comparable to the pre-FGD treatment system. In addition, particulate removal is similar in both systems, but the FGD process has the advantage of less spray nozzle plugging, which helps control both of the above.

Dual Alkali Dryer Scrubber Oxidation Rate Control Test

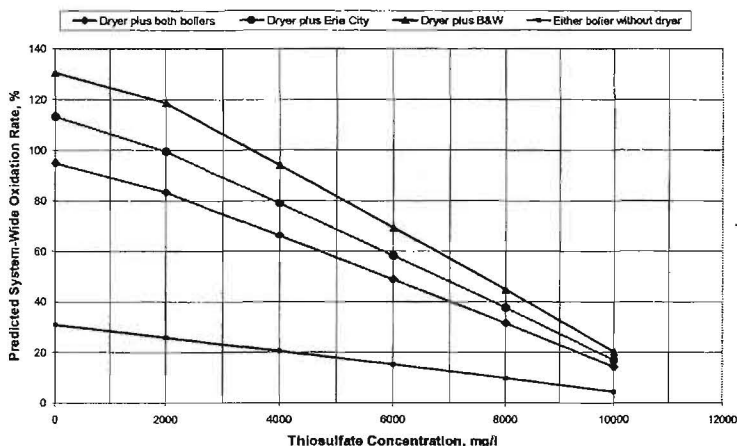
The next trial occurred in January of 2005 which consisted of reincorporating the dryer into the FGD system. The goal of this trial was to reduce/inhibit the high oxidation rate across the dryer scrubbers. Thiosulfate has been used in other FGD systems for this exact purpose since it interrupts the free-radical formation step in the oxidation process. Due to ease of handling for this trial, a 30% sodium thiosulfate solution was utilized. The thiosulfate was pumped into the dryer scrubber effluent pit just previous to being pumped to recycle and to the FGD system.

A most significant finding, which correlates to the full-scale experience of tying in the dryer to the FGD process, was that without thiosulfate, the dryer scrubbers oxidized not only the new SO₂ absorbed in the scrubbers, but also much of the sulfite in the clarifier overflow. Once the thiosulfate was added, the oxidation rate dropped in proportion to the thiosulfate concentration in the scrubbing liquor.

The dual alkali process will operate well if the system-wide oxidation rate is 30% or lower. The test results show that if the thiosulfate concentration is above about 9,500 mg/l, then the system oxidation rate will be acceptable. In addition, residual thiosulfate will inhibit oxidation rate in the boiler scrubbers. See the graph below of the oxidation rate versus thiosulfate concentration.



Predicted Oxidation Rates With the Use of Thiosulfate
 Mini-Cassia Dual Alkali FGD Process - January 2005



Chemical costs to control oxidation rate are acceptable. Utilizing elemental sulfur to generate the thiosulfate ($S + SO_3^- \rightarrow S_2O_3^-$) will cost around \$40 per day (\$80 per day using emulsified sulfur).

Mini-Cassia Dual Alkali FGD Operating Costs

The following table compares the previous scrubber water treatment daily costs to the FGD estimated daily costs. The FGD costs, since the dryer has not been permanently introduced into the FGD system, have been increased over the actual costs by the ratio of additional coal burned in the dryers.

Parameter \$ per day	Lime	Soda Ash	Power	Sulfur (S ₂ O ₃)	Scale Control	Sludge Handling	Total*
Old Lime Pond	\$67	\$0	\$134	\$0	\$1,401	\$21	\$1,623
Dual Alkali FGD	\$592	\$159	\$183	\$80 (Estimate)	\$392	\$357	\$1,763

FGD Increased Cost = \$140/day

*Does not include maintenance cost comparison

Dryer Scrubber Water Flume Water Treatment

During a portion of the time that the FGD system was treating only the boiler scrubber water, the pulp dryer scrubber water was diverted into the beet flume water system. This has proven to be successful at other factories and was also attempted at Mini-Cassia. Disadvantages include additional lime requirements to the flume, increased flume temperature and potential flume system scaling. However, the most critical disadvantage that the dryer scrubber

water produced was severe impedance of the settling of the beet dirt out of the beet flume water. This seems to be caused by a large infection in the mud settling pond. The infection generated significant quantities of foam and gassing. This method has been discontinued.

Conclusion

The Dual Alkali FGD system has proven to be successful in controlling the coal combustion emissions from the boiler wet scrubbers. The system has been reliable, and with further testing with thiosulfate chemistry, the pulp dryer wet scrubber water will be incorporated into the FGD system with no perceived issues.

References:

1. Wilhelm, James H., "Dryer Oxidation Inhibition Study Using Sodium Thiosulfate", CODAN Associates, 2394 Charros Rd., Sandy, UT 84092
2. Kaplan, Norman "An Overview of Double Alkali Processes for Flue Gas Desulphurization" EPA Symposium on Flue Gas Desulphurization, November 4-7, 1974