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Mercury Removal and its Fate in Oxidant Enhanced Wet Flue Gas Desulphurization Slurry

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The IEA CLEAN COAL CENTRE's

*8th International Conference on Clean Coal Technologies
(CCT2017) - 8-12 May 2017, Cagliari, Italy*

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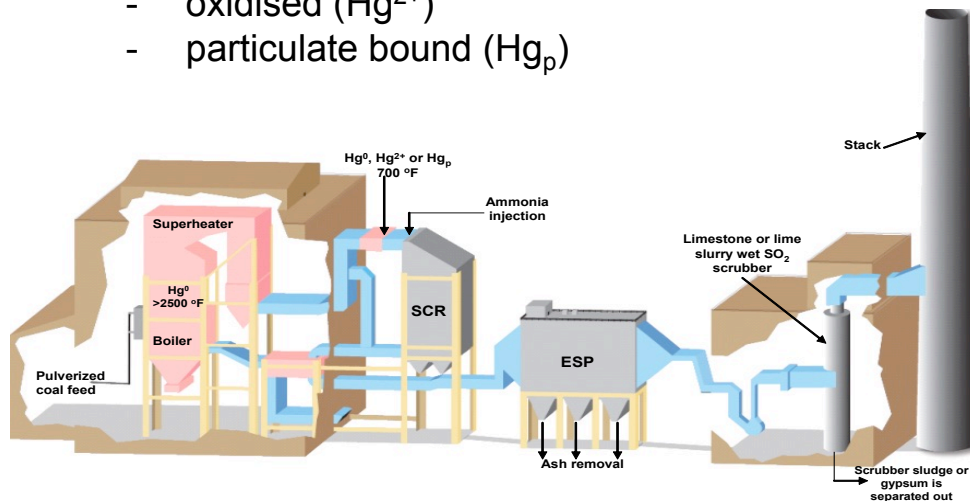


Mercury in flue gases – short summary

- ✓ Mercury concentrations in coal (even from the same deposit) strongly varies. Therefore mercury concentration in flue gas is variable also.
- ✓ Mercury exists in flue gas in three states:
 - elemental (Hg^0),
 - oxidised (Hg^{2+})
 - particulate bound (Hg_p)

- ✓ Mercury speciation is affected by:

- type of coal,
- concentration of sulphur and halogens in the coal,
- ash content,
- unburned carbon in the fly ash,
- flue gas temperature,
- residence time in particulate control devices,
- composition of flue gas,
- air pollution equipment in the post-combustion region of the boiler and by the air heater



- ✓ Mercury captured can be re-emitted from flue gas system !



Mercury technologies

There are a lot of different methods of mercury removal on different stage of development.

All existing technologies are based on physico-chemical processes: adsorption, absorption, oxidation, catalysis.

Understanding the chemistry beetwen mercury and other components is the key of every technology of mercury removal. It can help to avoid problems, excessive costs and make them more efficient.

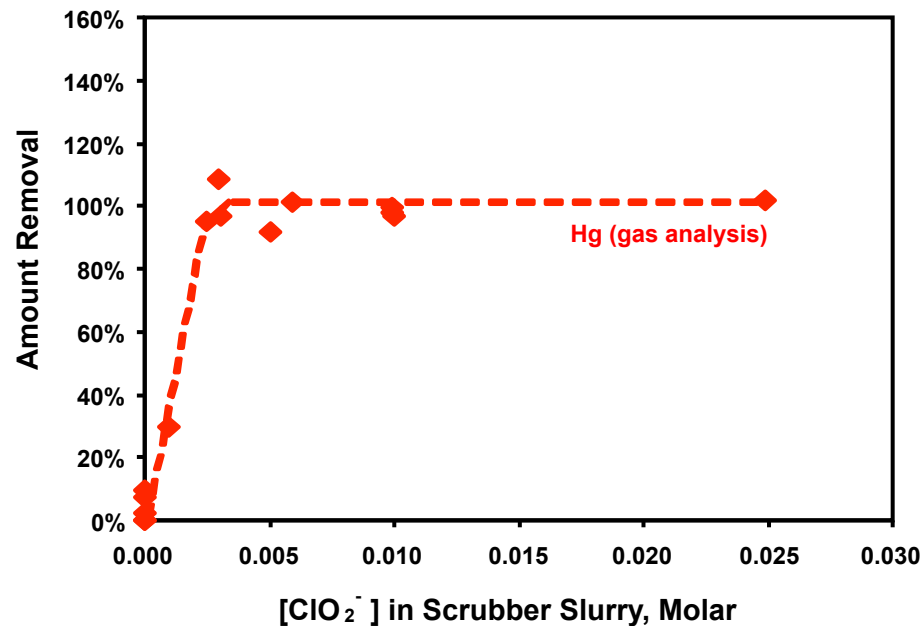
WFGD systems seem are good option for Hg capture why? ...

- ✓ Because wet flue gas desulfurization (WFGD) systems are commonly used all over the world, utilities for sulfur dioxide control to capture mercury, which exists in flue gases in “ug/m³” seems an obvious and rational choice.
- ✓ However, WFGD cannot directly scrub Hg⁰ efficiently, so it is necessary to find a cost-effective method to convert the Hg⁰ to an oxidized or even a particle-bound form before entering the WFGD system or in the scrubber. Conversion of Hg⁰ to Hg²⁺ or particulate-bound mercury can be accomplished by heterogeneous catalysis or homogeneous or heterogeneous gas-liquid phase oxidation.
- ✓ Injection of an oxidant into the flue gas (upstream of WFGD) or into WFGD to oxidize Hg⁰ appears to be the simplest method to implement.

Bench-scale tests

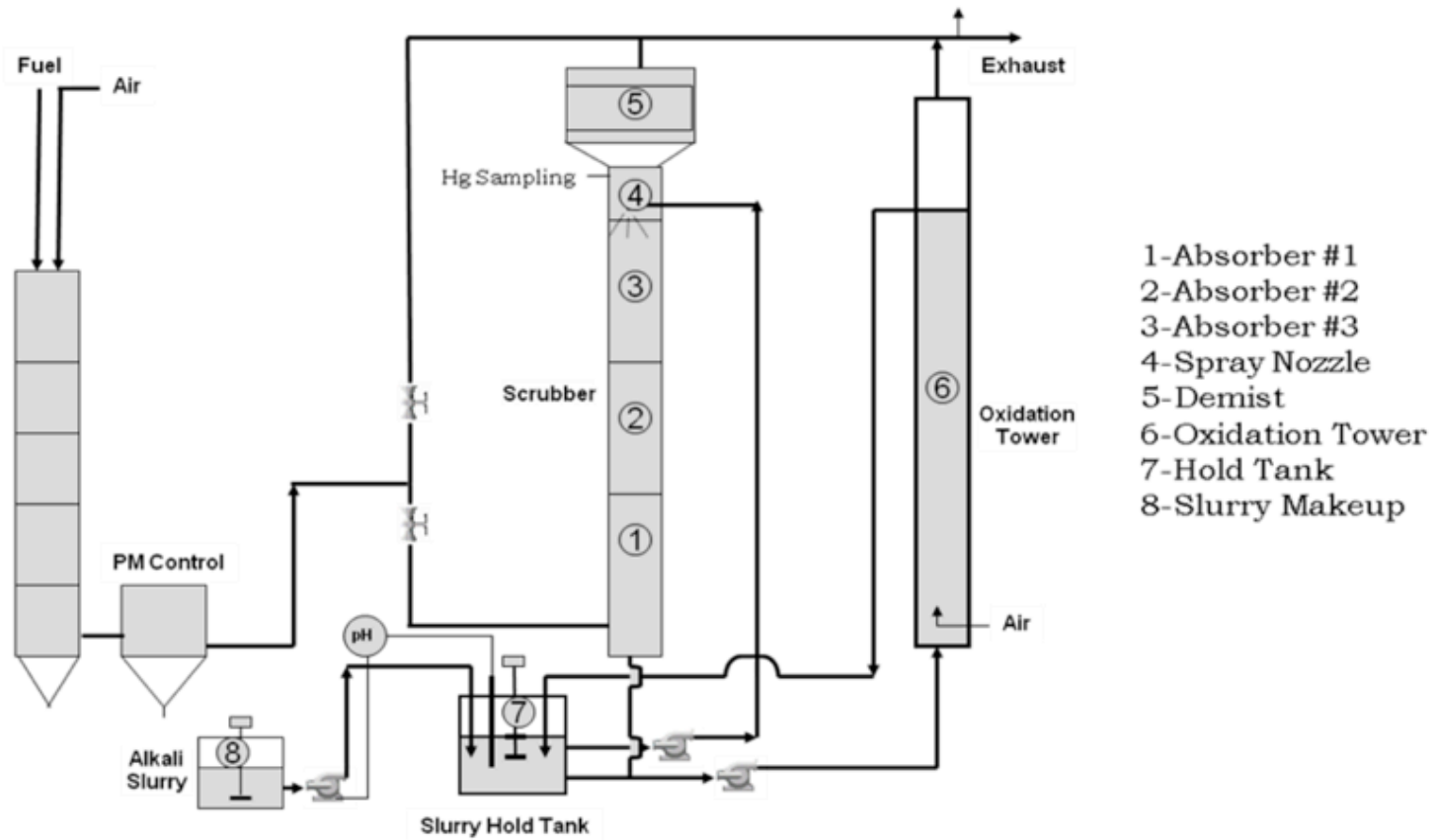
Variety of additives were tested (among them NaClO_3 , Ca(OCl)_2 , KMnO_4 , H_2O_2 , NaClO_2 , NaOCl)

The most promising was sodium chlorite



- Krzyzyska Renata, Hutson Nick D. 2012. Effect of solution pH on SO_2 , NO_x , and Hg removal from simulated coal combustion flue gas in an oxidant-enhanced wet scrubber. Journal of the Air & Waste Management Association, Vol. 62, Issue 2, p. 212-220.
- Krzyzyska Renata, Hutson D. Nick. 2012. The importance of the location of sodium chlorite application in a multi-pollutant flue gas cleaning system. Journal of the Air & Waste Management Association, Vol. 62, Issue 6, p. 707-716.
- Hutson Nick D., Renata Krzyżyńska and Ravi K. Srivastava. 2008. Simultaneous Removal of SO_2 , NO_x , and Hg from Coal Flue Gas Using NaClO_2 -Enhanced Wet Scrubber; Industrial & Engineering Chemistry Research, Vol.47, issue16, p. 5825 – 5831.

Pilot-scale research



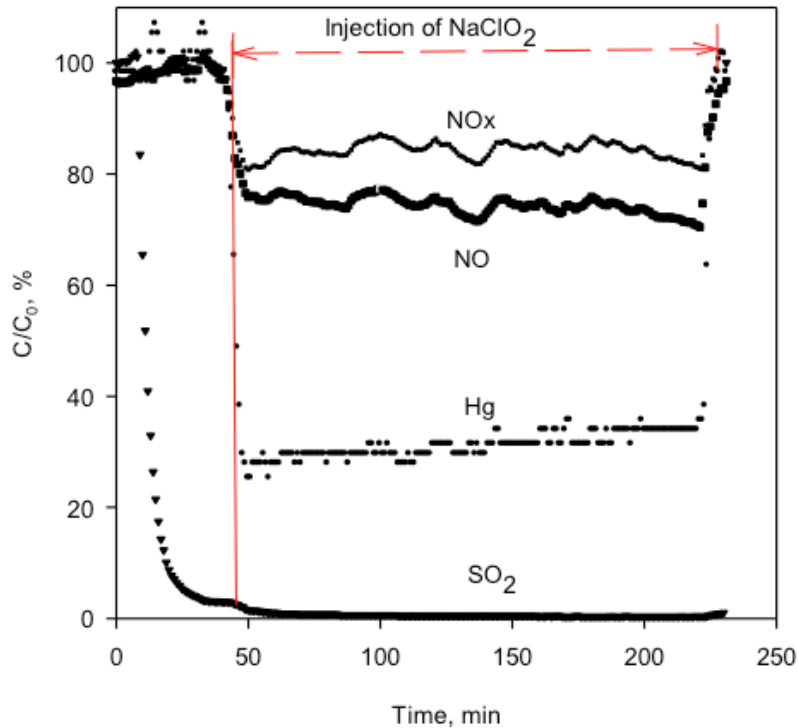
In this presentation I will focus on mercury removal from flue gas, discovering the fate of the captured mercury, with and without reagents, in wet scrubber and identifying the role which $\text{SO}_2(\text{g})$ and $\text{SO}_3^{2-}/\text{HSO}_3^-$ plays in mercury capture process. Research in pilot-scale installation.

Operating parameters

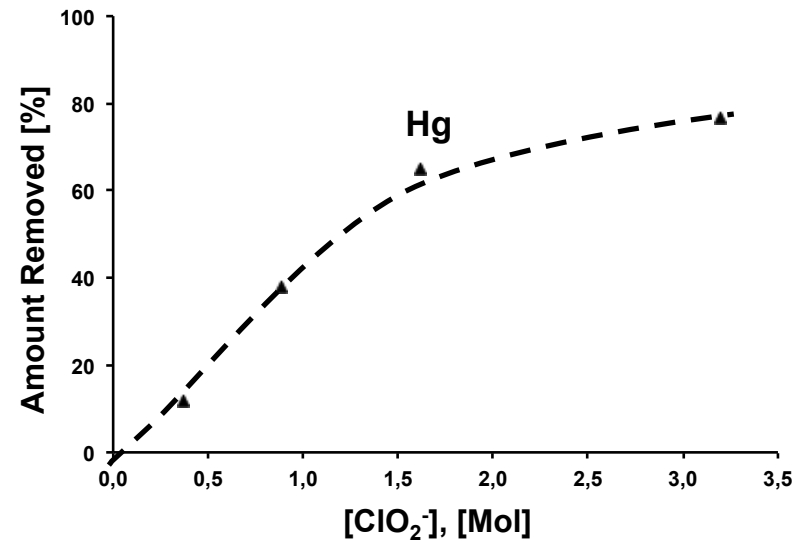
Experimental Condition	Parameter
Flue gas flow rate (G), L/min	800±50
Inlet flue gas SO ₂ concentration, ppm	550±50, 1100±100, 2000±200
Flue gas O ₂ concentration, %	7-8
Flue gas NO concentration, ppm	220±20
Flue gas CO ₂ concentration, %	6-7
Hold tank slurry volume (V), l	10±2
Hold tank pH	6.2±0.2
Slurry recirculation rate (L), L/min	8.0±0.5
Hold tank slurry temperature, °C	47±2
Hg concentration (C_0), µg/m ³	17±2
Air to oxidation tower, L/min	45
Oxidation tower volume, L	150

The concentrations of Hg, SO₂, and NO_x were monitored at both the scrubber inlet and outlet using continuous emission monitoring (CEM) systems. Measurements of Hg⁰ were performed using ultraviolet (UV) spectrometers (Seefeldler-Hg 3000). Hg in the scrubber liquor was measured, when required, by cold vapor atomic absorption (CVAA) analyzer following EPA method 7040A. The NO_x species were monitored by an NO_x analyzer (API model 200AH) while SO₂ was measured by a fluorescence analyzer (API model 100AH).

Pilot-scale demonstration

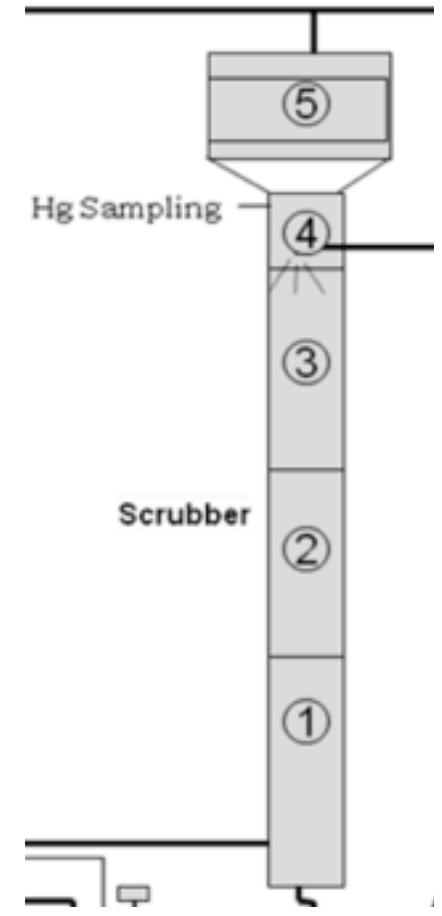
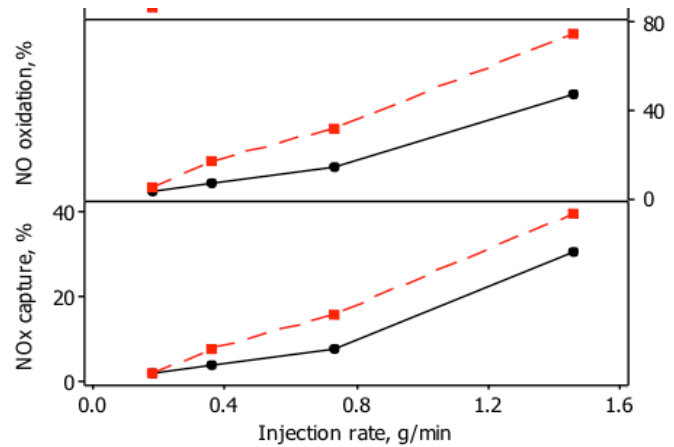
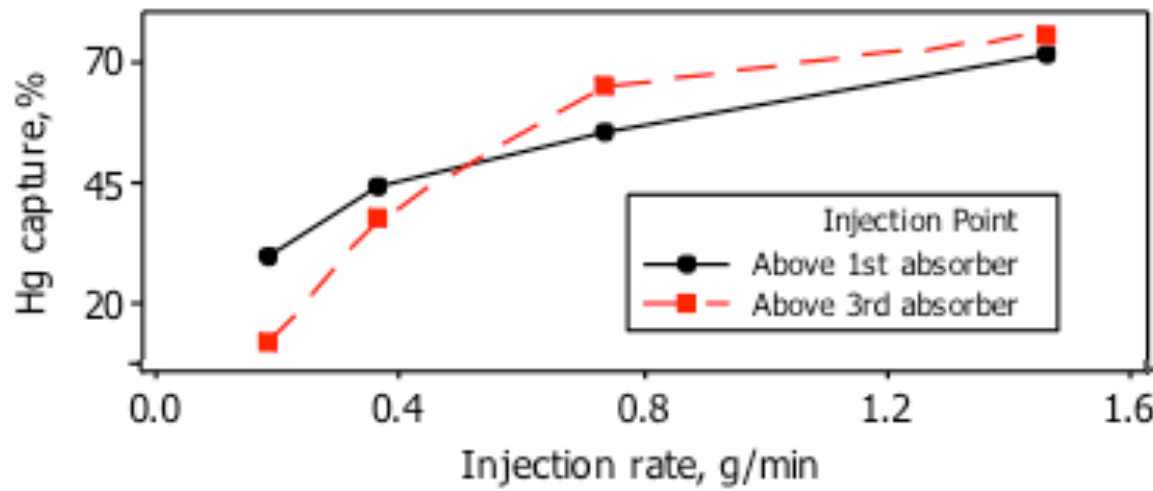


**$[NaClO_2] = 1.62$ M solution;
(0.98 mM in spray nozzle)
 $[SO_2] = 1100$ ppm**



**$[NaClO_2] = 0 - 3.2$ M
 $[SO_2] = 1100$ ppm**

Mercury and other Pollutant Capture with Different Injection Rates and Injection Points in the Scrubber



Mercury reemission from the classic wet limestone scrubber system

Wet-FGD limestone scrubbers – „NO OXIDANTS”

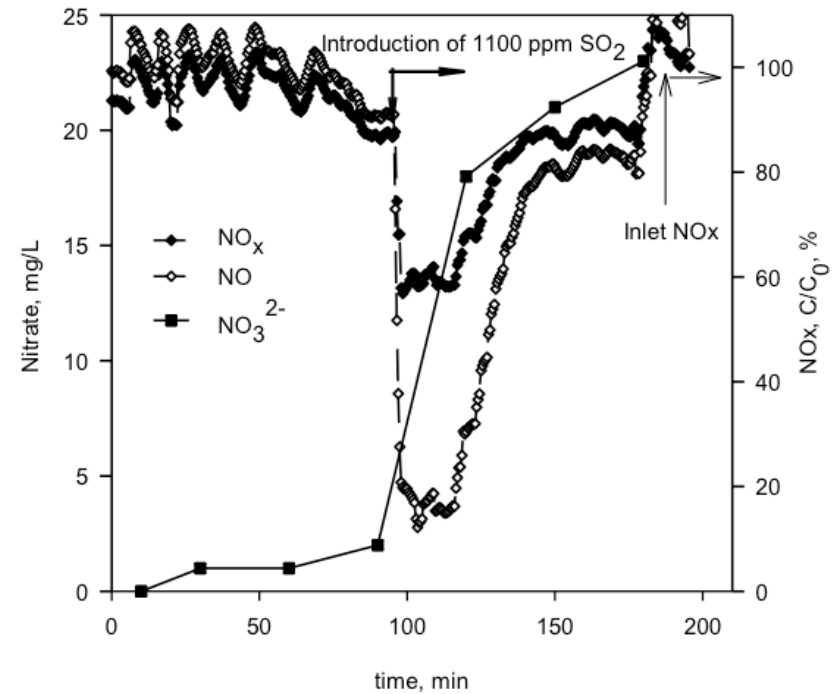
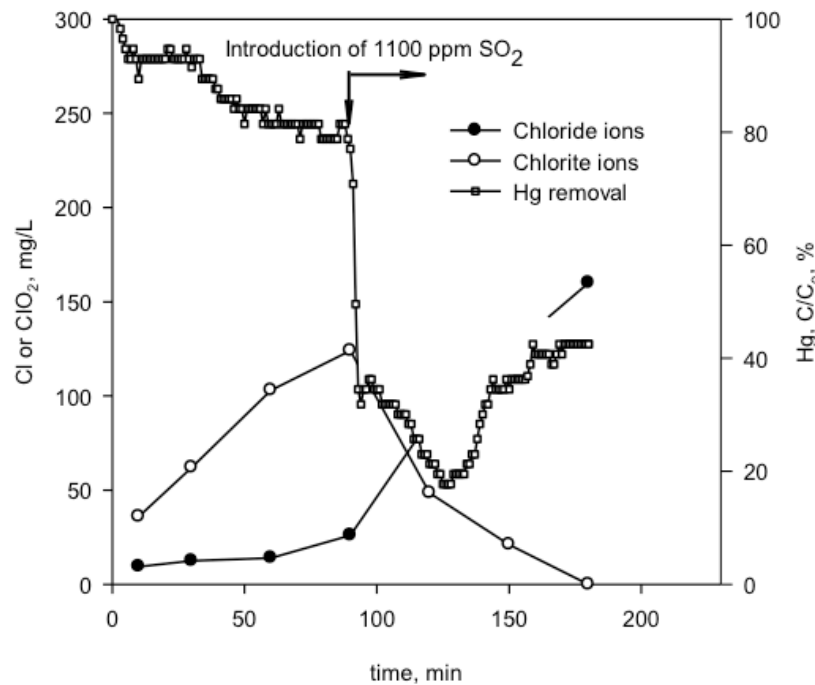
- ✓ In FGD scrubber systems significant amount of absorbed Hg^{2+} can be reduced by aqueous S(IV) (sulfite and/or bisulfite) species.
- ✓ Pilot plant data have also shown evidence for mercury reemissions outside the scrubber loop too. Temperature and disturbance (e.g.:mixing, pumping, bubbling, and vacuuming) can significantly affect the mercury reemission rate.
- ✓ Hg^0 reemission results in an increase of flue gas Hg^0 concentration across the scrubber by as much as 58% and significantly reduces the co-benefit.

Mercury reemission from the additive enhanced wet limestone scrubber

Wet-FGD limestone scrubbers – ADDITIVE ADDED

- ✓ mercury reemission from wet slurry, fed by sodium chlorite/calcium carbonate slurry was negligible (ab. 0.7 % of the added mercury)
- ✓ Negligible reemission was observed also from the forced oxidation tower.
- ✓ Presented research showed that the majority of Hg was retained in the liquid phase, consistent with the nature of such reagents as CaCO_3 , CaSO_3 , and CaSO_4 whose crystal structure is not conducive to absorbing Hg.

Impact of Sulfur Dioxide on Mercury and other Pollutant Conversions



Prior to the injection of SO₂, NaClO₂ (0.36 g/min) was first fed to the scrubber system for 90 minutes through the point at top of the absorber #3. In the absence of SO₂, the slurry pH was 7.4. SO₂ injection was turned on at the 90th minute. The pH of the slurry was then automatically maintained at 6.4 by the pH control system.

Impact of Sulfur Dioxide on Mercury and other Pollutant Conversions – cd.

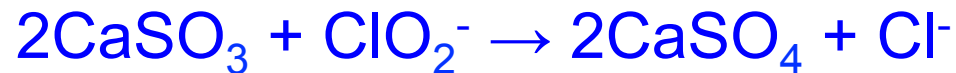
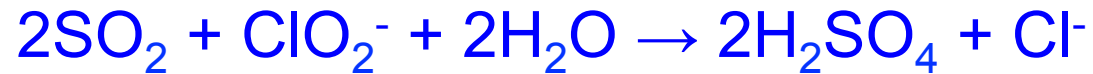
Impact of varying sulfur dioxide concentration on pollutant oxidation/capture

Injection rate (g/min)	SO ₂ Concentration, ppm	Hg Capture, %	NO oxidation, %	NO _x capture, %
0.36	550	50	9	6
	1100	37	17	8
	2000	10	4	4
0.73	550	65	29	14
	1100	65	33	17
	2000	50	18	11



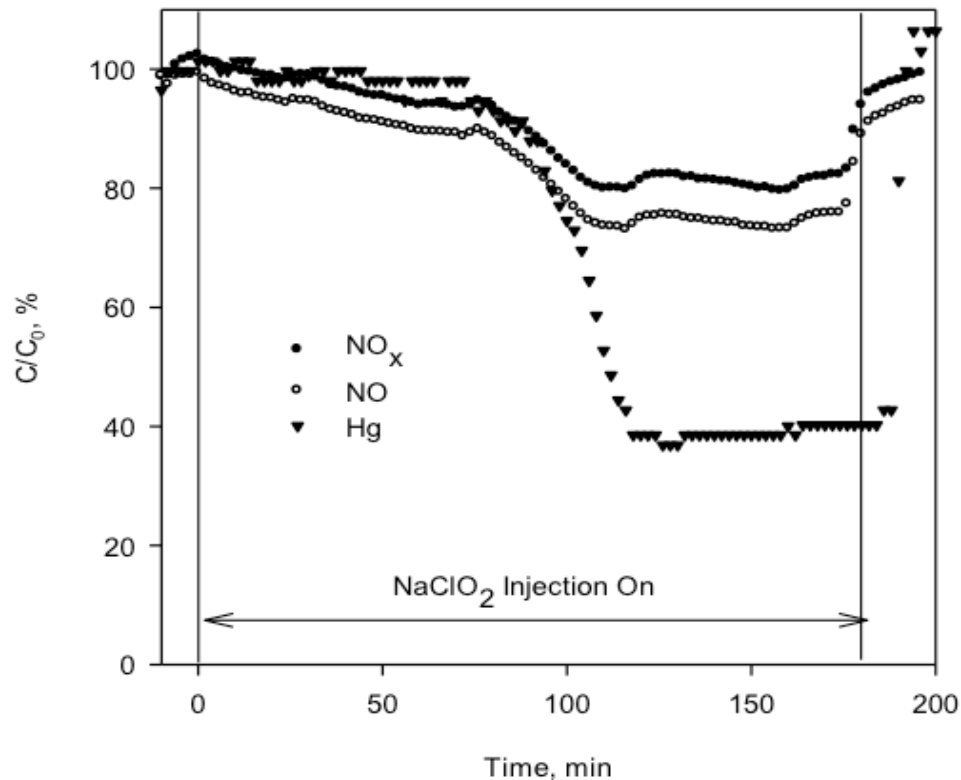
To what extent does the gaseous SO_2 contribute to NaClO_2 depletion?

It is not clear whether the depletion is caused primarily by gaseous SO_2 or though aqueous SO_3^{2-} as shown in Equations:



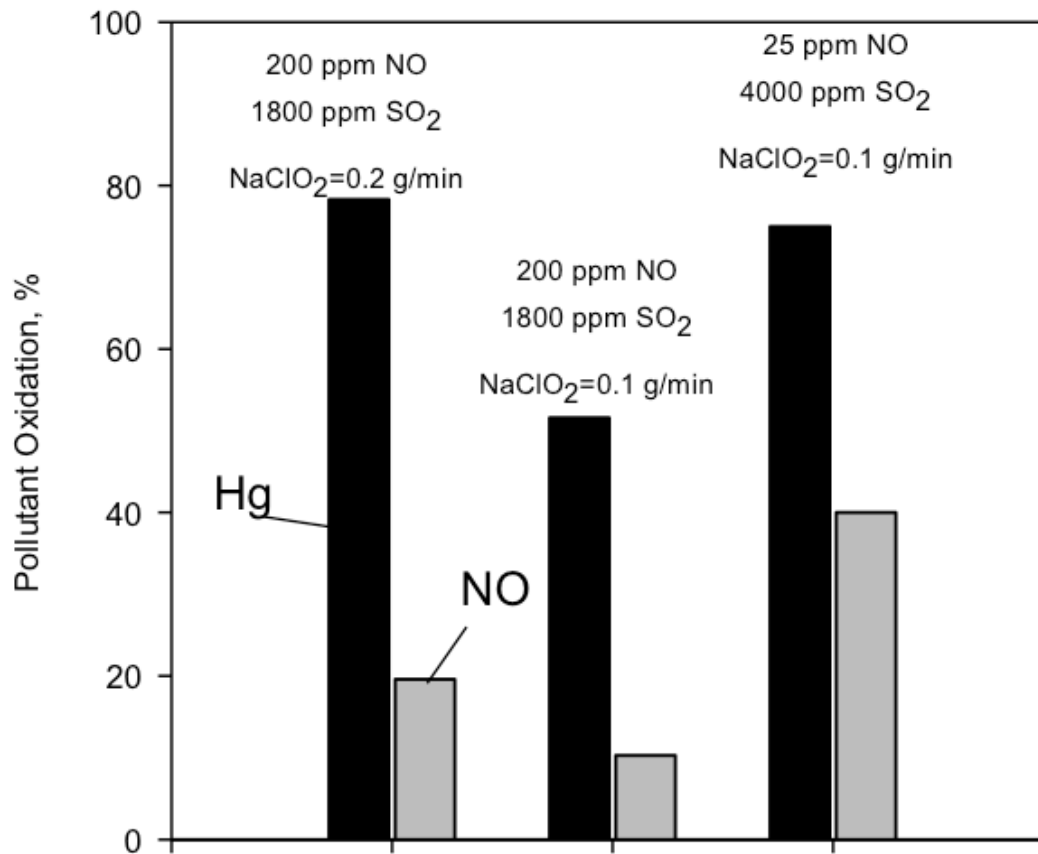
Impact of $\text{SO}_3^{2-}/\text{HSO}_3^-$

To validate the adverse impact of liquid $\text{SO}_3^{2-}/\text{HSO}_3^-$, an additional run was conducted by turning off the air to the forced oxidation tower. In this way, $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions in the slurry were built up because of a slower natural oxidation. This process was continued for 90 minutes. When $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions were built up, its concentration in the absorber #3 would be much higher than that under the forced oxidation mode.



Pollutant capture under natural oxidation operation mode ($\text{SO}_2=2000$ ppm in the flue gas, 0,73 g/min. NaClO_2).

Impact of $\text{SO}_3^{2-}/\text{HSO}_3^-$ - additional series of experiments



- Results were comparable magnitude to those when adding NaClO_2 directly to scrubbing slurry because of the avoidance of liquid NaClO_2 and $\text{HSO}_3^-/\text{SO}_3^{2-}$ reaction.
- Clearly, by injecting NaClO_2 before the wet scrubber, the NaClO_2 usage can be substantially slashed, while the same or higher level of pollutant control can still be reached.
- For comparison purpose, the demanded amount of NaClO_2 was substantially brought down by 73 to 87%.



Conclusions

- ✓ Basing on Authors earlier presented results, it was confirmed in pilot-scale research that mercury can be removed in wet flue gas desulphurization systems together with other pollutants (SO_2 , NO_x), when absorber slurry is enhanced by proper selected additive.
- ✓ Mercury reemission from wet slurry, fed by sodium chlorite/calcium carbonate slurry was negligible (as opposed to those without additives). Negligible reemission was observed also from the forced oxidation tower.
- ✓ The majority of Hg was retained in the liquid phase.
- ✓ It was discovered, that not SO_2 , but $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions play important role in consuming oxidizer.
- ✓ Mercury doesn't need long residence time to react with sodium chlorite. The results showed that more important factor are concentration of $\text{HSO}_3^-/\text{SO}_3^{2-}$ ions. This finding can help us and other researchers in future to develop such and similar methods of mercury removal.
- ✓ It's worth to remember that mercury is a complex issue and all methods of mercury removal need to deeply understand the chemistry, and all parameters, especially in pilot and full-scale. One can avoid unnecessary additional cost&problems in real power plant.



THANK YOU FOR YOUR ATTENTION!

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