

Studies of Fates of Sulfur Trioxide (SO₃) in Coal-Fired Utility Boilers Based on Modified Selected Condensation Methods

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S1. Standard methods of SO₃ sampling.

EPA method 8 is primarily designed to collect SO₃ in a gas stream from a sulfuric acid plant, where the SO₃ concentration is generally high compared to SO₂ and where there is no moisture or other pollutants in the gas stream. This method uses 80% isopropyl alcohol (IPA) as a trapping solution for gaseous SO₃. Un-trapped SO₃ mist is collected by the follow-up filtration trap. This method's major problem is that SO₂ could be soluble in an 80% IPA solution, although this solubility is limited. This is not acceptable when this method is applied during SO₃ collection in coal-fired utility boilers, where concentration of SO₂ is much higher than SO₃ in the coal-fired flue gas. The collected SO₂ will be incorrectly calculated to be SO₃ and thus creates a greater positive bias on SO₃ measurements. This has been confirmed in our laboratory tests. A simulated flue gas was prepared with 1588 ppm SO₂, 4.93 % of O₂ and 13.73 % CO₂, balanced by nitrogen (N₂). Tests were conducted by applying this simulated flue gas with a flow rate of 100 ml/min from 30 minutes to 75 minutes. The result in Table S1 shows that SO₂ or the conversion of SO₂ into SO₃ was not found in 100 % IPA solution, but was found in the 80 % IPA solution under the same test conditions. This test confirmed that IPA is not responsible for SO₂ trapping or conversion, but that water in the IPA solution traps SO₂. Considering its ease of handling, the 100 % IPA solution still holds merit for selective collection of SO₃ in that we could use this method in a lab-scale SO₃ adsorbent evaluation test using a moisture-free simulated flue gas. Another positive bias is created by the filter-captured sulfate or sulfite salts in the coal-fired flue gas, which will also be incorrectly calculated to be SO₃. On the other hand, the temperature in the sampling probe by this method is about 125 °C, which is well below the dew point of SO₃ in the coal-derived flue gas. Therefore, a negative bias might be created due to condensation of SO₃ in the sampling probe.

ASTM Controlled Condensation Method (ASTM 3226-73T) is specially designed to collect SO₃ in coal-derived flue gas. The principle of this method is to separate SO₃ from

SO₂ based on the maximum difference in condensation kinetics of SO₃ and SO₂ at around 60 to 65 °C. The SO₃ sampling probe is set at about 260 °C, and thus, eliminates the negative bias from the condensation of SO₃ in the sampling probe. However, our experience indicated that a higher filtration temperature would likely have a negative bias. Filtered fly ash will likely collect SO₃ in the gas stream before it enters the SO₃ condenser.

EPA method 17 is a standard method to define a procedure of flue gas sampling based on in-stack filtration, by which fly ash and clean gas is separated.

Due to the adverse effect of the fly ash adsorption on the accuracy of the SO₃ measurement, EPA's method 8A has been developed to move the original location of the filtration system from the front of the sampling probe to the end of the probe, where filtration temperature control can be flexible depending on the specific site. The temperature of the filtration system is as high as that of the probe at 180 °C. Therefore, fly ash adsorption on the sampling filter will likely be minimized. However, the interference between fly ash and SO₃ in the flue gas is not so simple. Some inorganic constituents in fly ash are ready to react with SO₃ with varied kinetics under different temperatures. Some constituents in fly ash are also likely to decompose and thus emit SO₃ into the gas phase in the sampling train. The positive or negative bias may occur in SO₃ sampling, depending on a host of reasons.

S2. Lab-scale reactor.

Lab-scale fixed-bed tests with selected fly ashes and one commercial CaO-based SO₃ adsorbent were conducted to evaluate the previously mentioned two-way interaction (adsorption and reaction) between fly ash and SO₃ and its transition in the SO₃ sampling train. The one gram of fly ash was loaded in this fixed-bed reactor, with which SO₃ and moisture-laden air passed in a flow rate of the gas stream at 100 ml/min. This SO₃ and moisture-laden gas stream was made possible by injection of sulfuric acid water solution into an air stream at a decomposer, whose temperature was about 350 - 400 °C. At this

temperature, the sulfuric acid solution is supposed to decompose as SO_3 and steam. The SO_3 concentration in the gas stream varied between 8.4 ppmv and 33.6 ppmv, which were typically found in coal-derived flue gas in the utility boilers. The moisture content varied between 10 - 20 %, which was presented as moisture content of three typical U.S. coals (bituminous coal, sub-bituminous coal and lignite). During tests, the temperature of the fixed bed was controlled between 150 - 350 °C to simulate typical temperature ranges of flue gas after the SCR in a utility boiler. To simplify SO_3 measurements, EPA Method 6 setup was applied since it was confirmed to be accurate in SO_3 measurements for gas streams free of SO_2 and moisture. The setup of EPA Method 6 included two impingers with 3 % hydrogen peroxide (H_2O_2) in an ice water bath. Prior to testing, a blank test was conducted to ensure the right SO_3 concentration in the gas stream. Simultaneously, the recovery of SO_3 downstream of the fixed bed by the selected SO_3 collection method was generally found to be above 90 %. The SO_3 removal efficiency, after fly ash was loaded in the fixed bed during different conditions, was calculated by the difference of the total SO_3 mass at the inlet of the gas stream and that at the outlet of the gas stream.

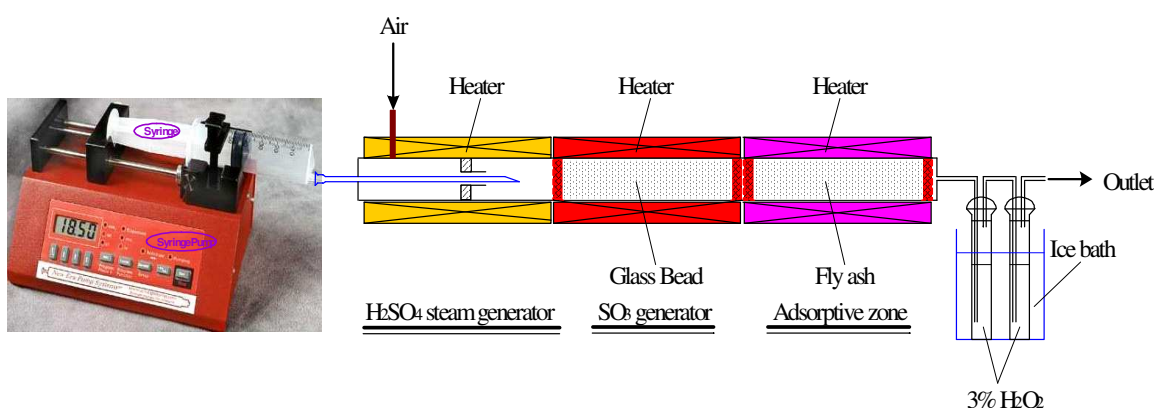


Fig. S1. Lab-scale Fixed Bed Reactor

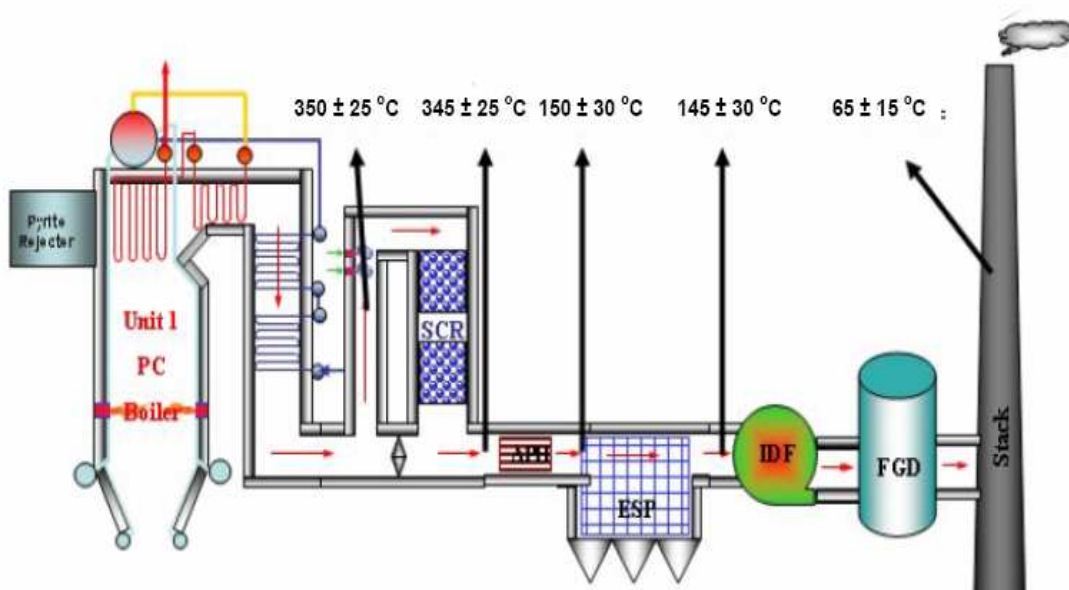


Fig. S2. Schematic of three-testing unit configuration.

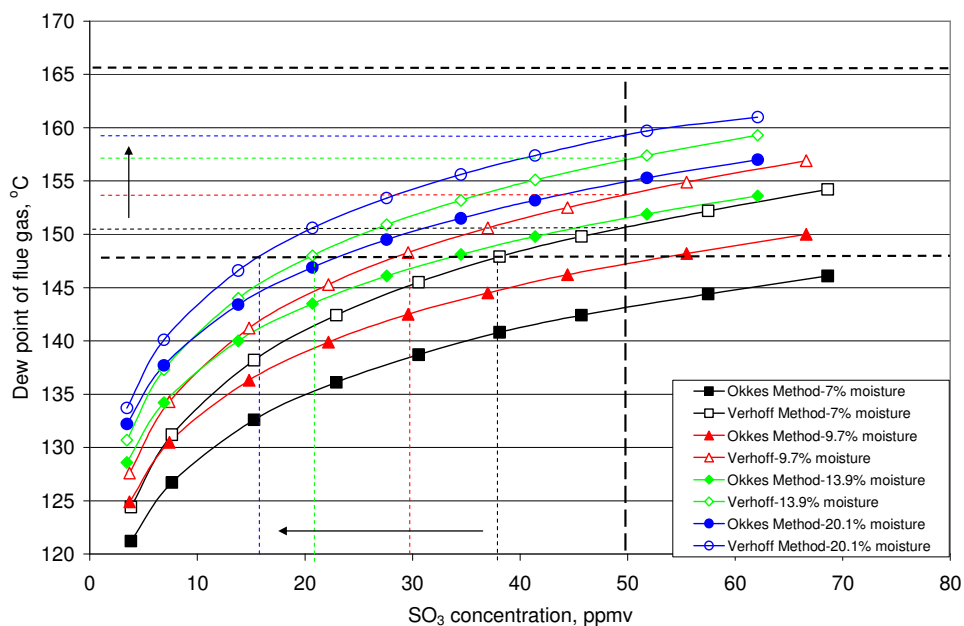


Fig. S3. The predicted dew point of SO₃ in the flue gas.

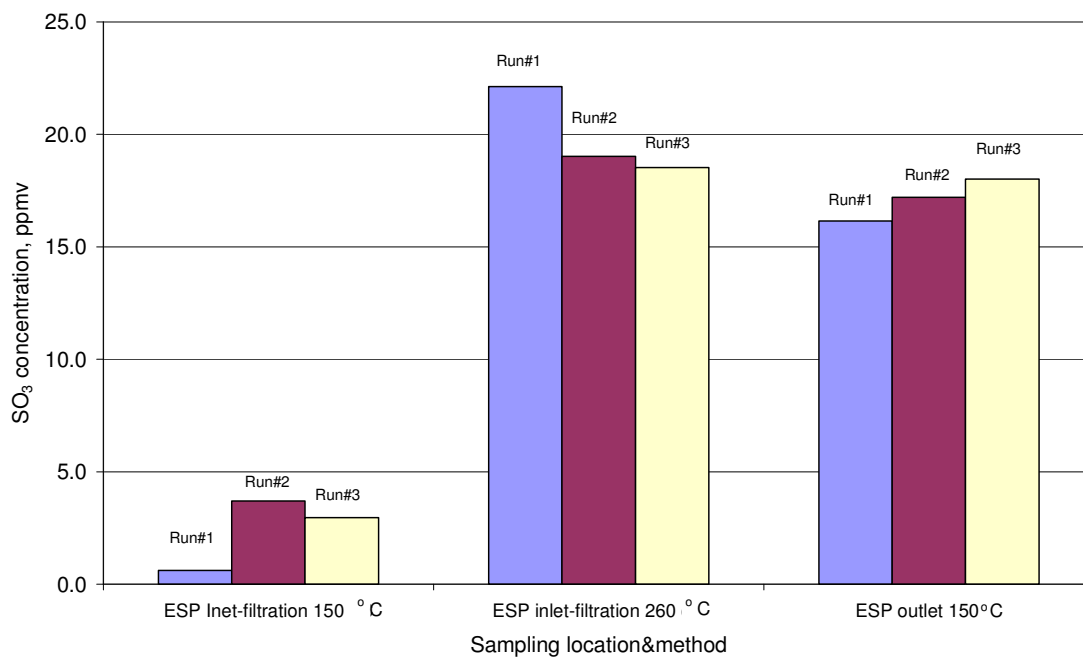


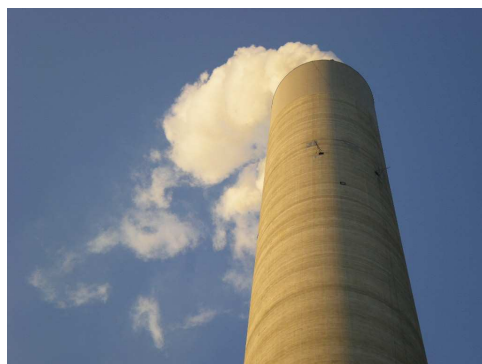
Fig. S4. Effect of fly ash at ESP inlet location on SO₃ measurement.



Stack at Site #1



Stack at Site #2



Stack at Site #3

Fig. S5. Stack plume at three testing sites

Table S1. Comparison of SO₂ capture by 100 % and 80 % IPA solutions

Test Conditions			
	SO ₂ source	SO ₂ : 1588 ppmv, O ₂ : 4.93%, CO ₂ : 13.73%, N ₂ balanced	
	Temperature&Pressure	273.15 °K (ice water), 1 bar	
	Source gas flow rate	100 ml/min	
Test No.	Methods	IPA solution SO ₄ ²⁻ verse total SO ₂ in IPA and H ₂ O ₂ solutions	recovery rate of the total SO ₂
1	100% IPA solution	<0.01%	96.4%
2	100% IPA solution	<0.01%	111.7%
3	80% IPA solution	2.04%	100.4%
4	80% IPA solution	1.96%	95.8%

Note: A recovery rate over 100% may have resulted from the overestimate of solution volume after tests, which should be slightly less because of the carrying effects of gas during tests.

Table S2. Proximate and ultimate analysis of coal tested in three testing sites

Sample Name	Dry Basis												
	ADL	Moisture	Ash	Vol. Mat	Sulfur	Btu	Carbon	Hydrogen	Nitrogen	Oxygen	Chloride	Mercury	Fluoride
Sample Name	%	%	%	%	%	BTU/lb	%	%	%	%	ppm	ppm	ppm
Site 1 - bituminous coal	4.12	1.04	14.10	36.29	3.74	12918	71.23	5.06	0.76	5.12	595	0.10	94
Site 2 - bituminous coal	5.60	2.04	11.92	36.60	3.57	13009	73.98	4.98	0.81	4.74	454	0.13	92
Site 3 - Sub-bituminous coal	9.69	28.47	7.47	46.69	0.41	11656	67.82	9.32	0.48	14.50	43	0.08	62
Sample Name	Mercury	Sulfur	LOI	Chloride	Fluoride								
	ppm	%	%	ppm	ppm								
Site 1 - bituminous coal	0.10	0.54	1.98	151	ND								
Site 2 - bituminous coal	0.01	0.31	2.19	457	33								
Site 3 - Sub-bituminous coal	0.20	0.51	0.56	59	108								
Sample Name	H ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	K ₂ O	SO ₃	P ₂ O ₅	BaO	SrO	Fe ₂ O ₃	MnO	TiO ₂
	%	%	%	%	%	%	%	%	%	%	%	%	%
Site 1 Bituminous coal ESP Ash	0.55	1.30	21.75	50.82	4.20	2.53	0.71	0.25	0.17	0.14	16.25	0.03	1.30
Site 1 Bituminous coal Economizer Ash	0.15	1.13	22.32	49.88	3.02	2.34	0.34	0.12	0.16	0.10	19.24	0.03	1.16
Site 2 bituminous coal Economizer Ash	0.00	0.82	19.43	45.90	3.41	2.07	0.59	0.20	0.07	0.06	26.31	0.03	1.14
Site 2 bituminous coal APH Ash	0.11	0.97	21.85	47.07	2.51	2.13	2.04	0.40	0.05	0.04	21.83	0.03	1.00
Site 2 bituminous coal ESP Ash	0.07	0.77	21.96	49.67	2.56	2.08	0.56	0.28	0.07	0.08	20.65	0.02	0.89
Site 3 - sub-bituminous coal ESP ash	1.16	4.65	17.67	40.00	25.4	0.58	1.85	0.99	0.62	0.42	5.27	0.02	1.38