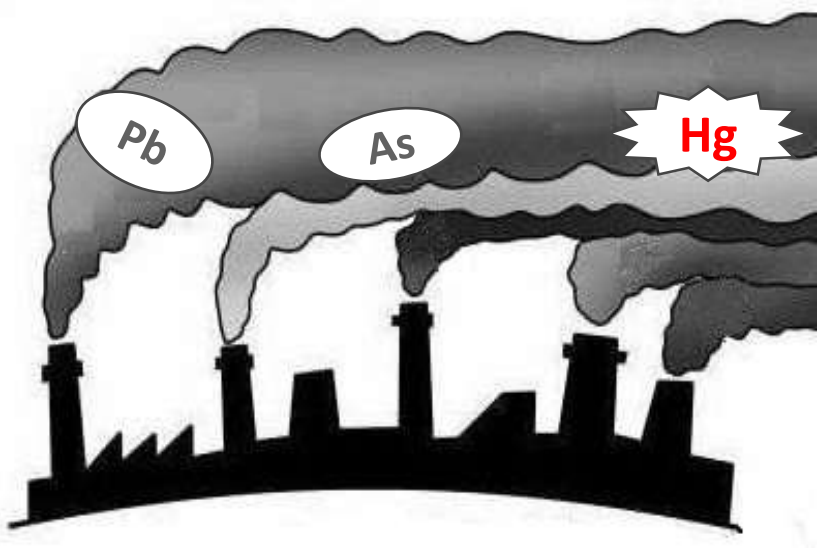
The migration and species transformation of Hg in wet flue gas desulfurization system

Yongchun Zhao 赵永椿

Email: yczhao@hust.edu.cn

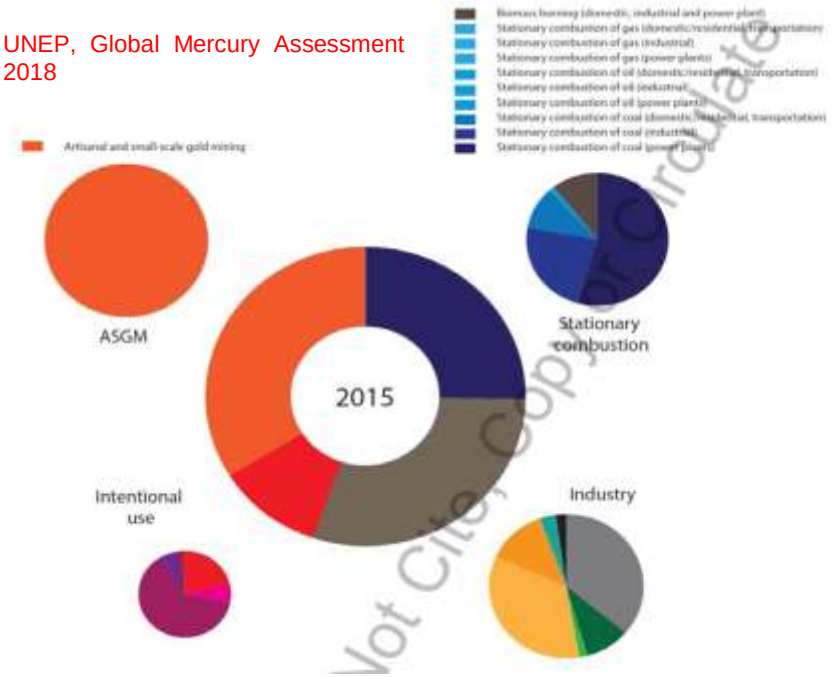
State Key Laboratory of Coal Combustion
National Environmental Protection Engineering Technology Center for Trace Elements Pollution Control and Low Carbon Utilization of Coal
Huazhong University of Science and Technology, Wuhan, China

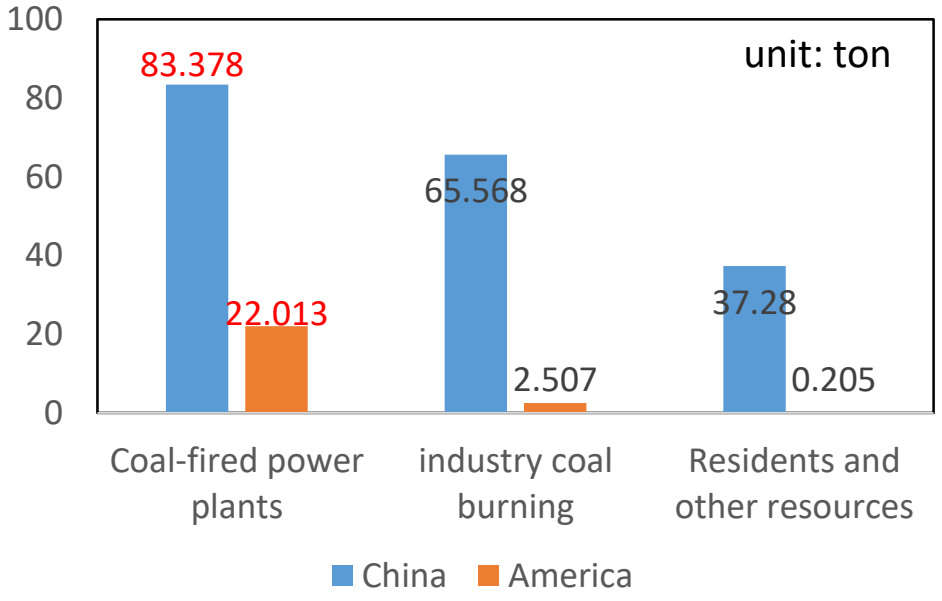
Background



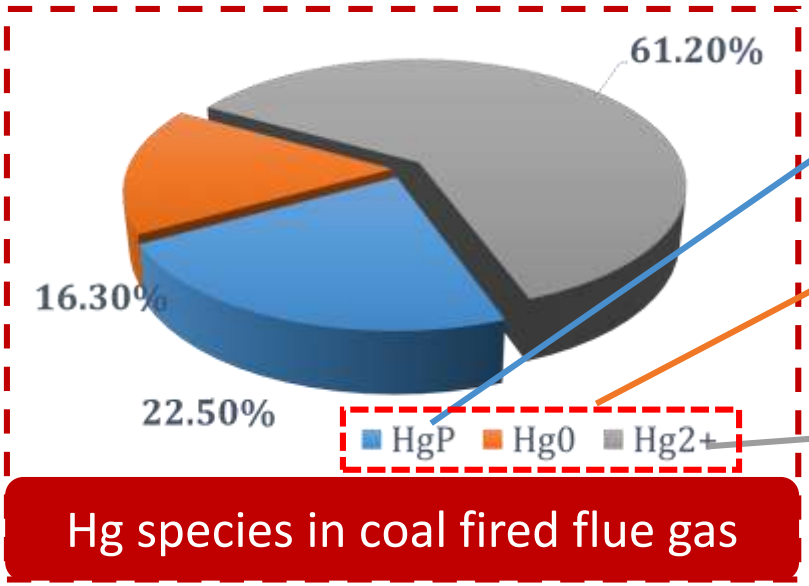
- In China, coal consumption was 3783 Mt in which coal-fired power plants account for over 50% of this total in 2016.
- Global anthropogenic Hg emission reached up to 2220 t in 2015. The amount of Hg emission by coal-fired power plants in China was 83.378 t, while it was 22.013 t for America in 2015.

UNEP, Global Mercury Assessment 2018





Hg in flue gas

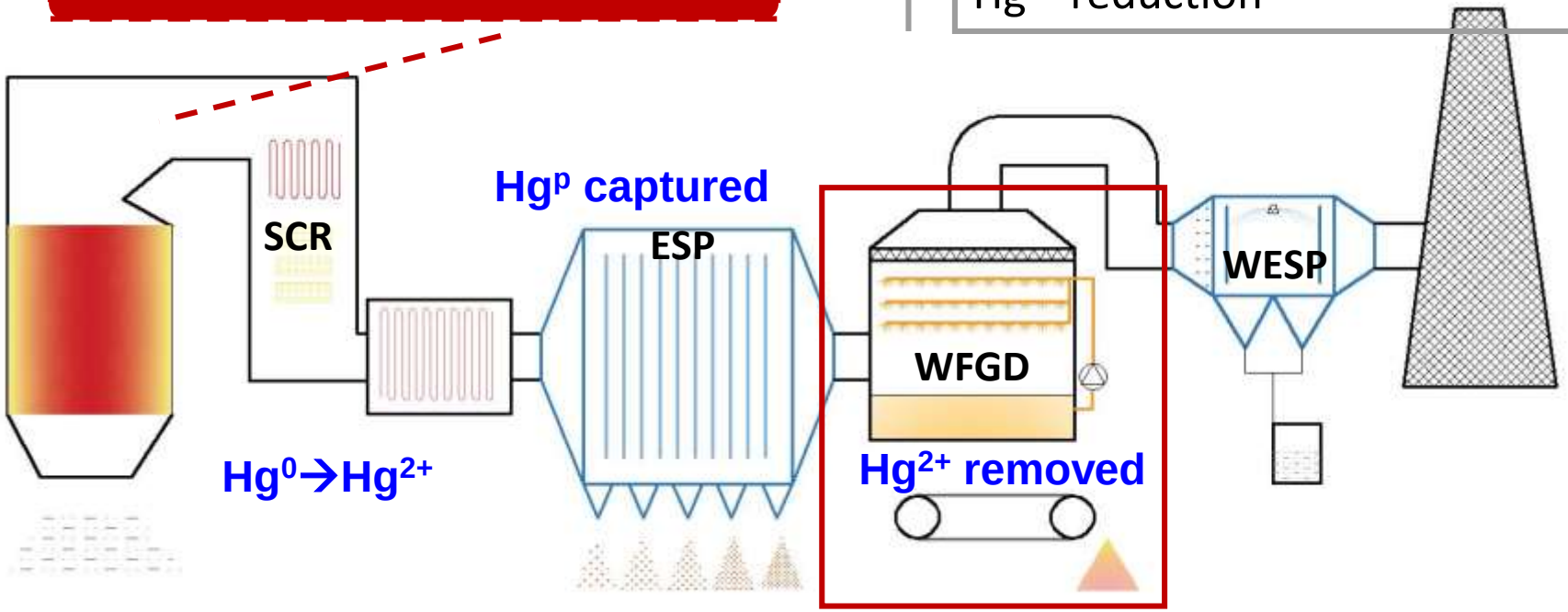


Hg species in coal fired flue gas

Hg^P, particle-bound Hg, removed by ESP efficiently

Oxidized by SCR catalyst

Hg^{2+}, water-soluble, can be removed by WFGD.
Unexpected re-emission via Hg^{2+} reduction



WFGD system

Desulfurization tower

Flue gas inlet

Flue gas outlet

pH adjustment

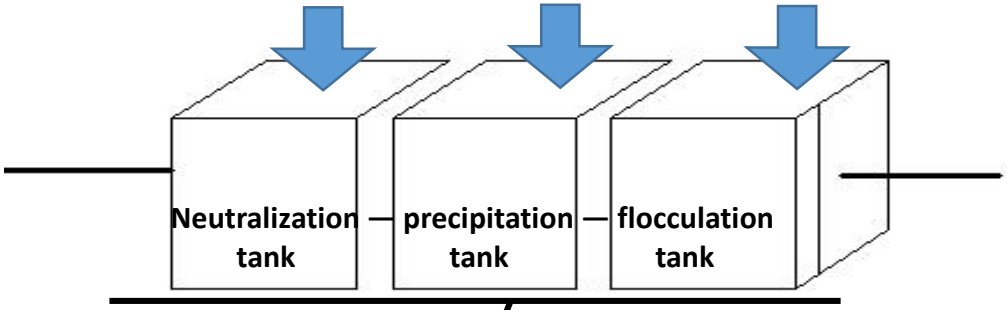
Fe-OH precipitation

Flocculation enhancement

Hydrated lime

$FeClSO_4$

PAM



Three-linked tanks

Gypsum hydrocyclone

Filtrate tank

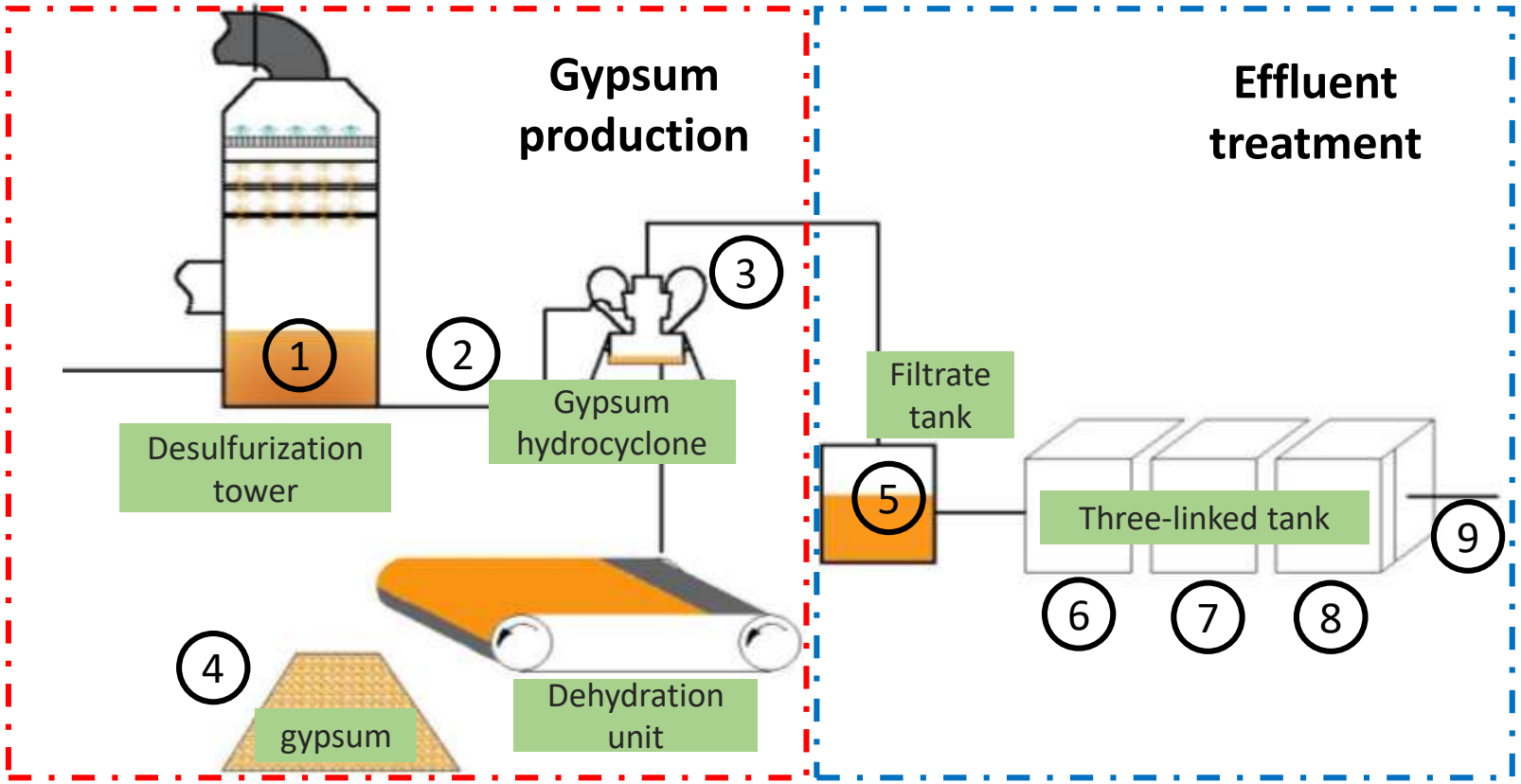
Dehydration unit

Effluent hydrocyclone

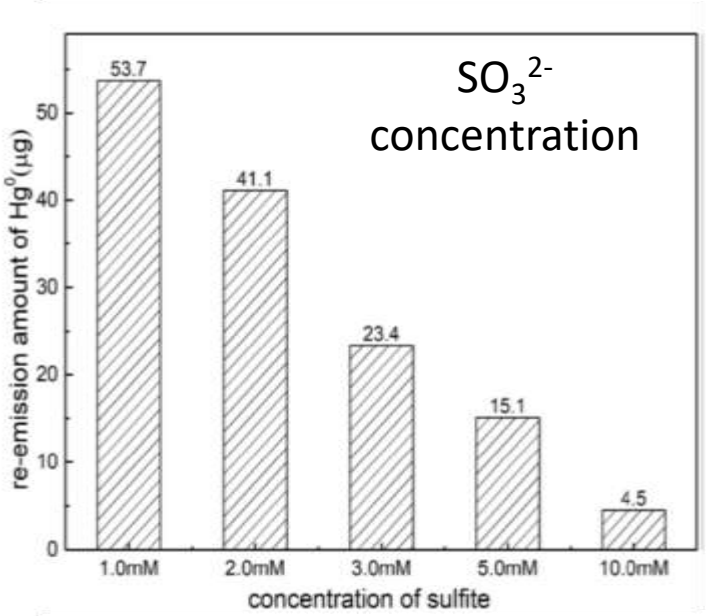
Onsite sampling

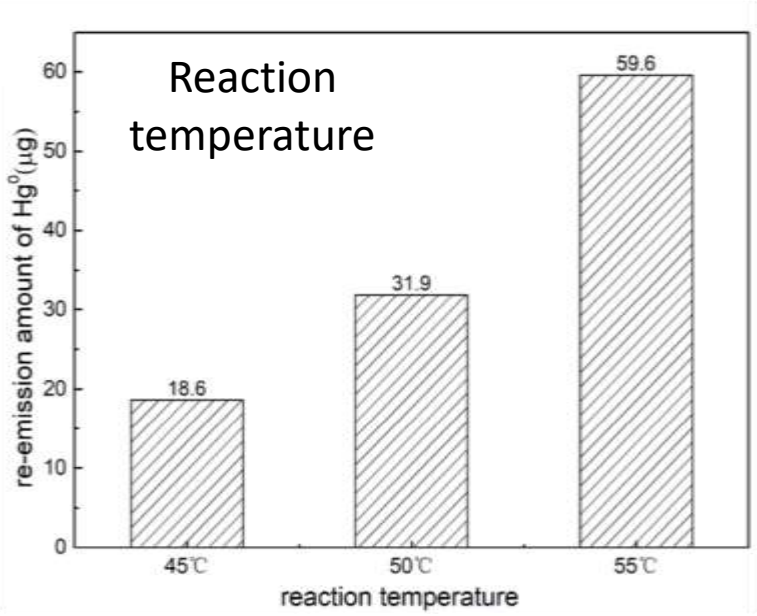
Samples information： 4×300MW coal-fired power plant

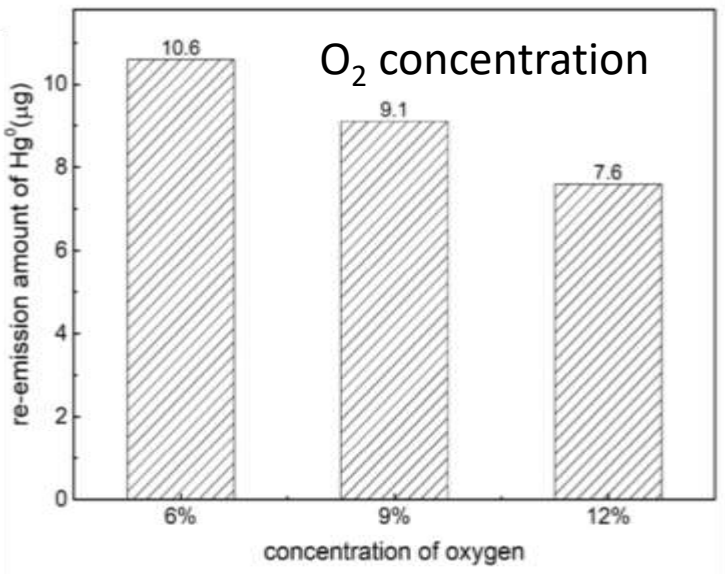
- Gypsum production： 1. desulfurization slurry 2. gypsum slurry 3. Gypsum hydrocyclone slurry 4. gypsum
- Effluent treatment： 5. effluent 6. neutralization slurry 7. precipitation slurry 8. flocculation slurry 9. drainage



Hg re-emission in desulfurization slurry

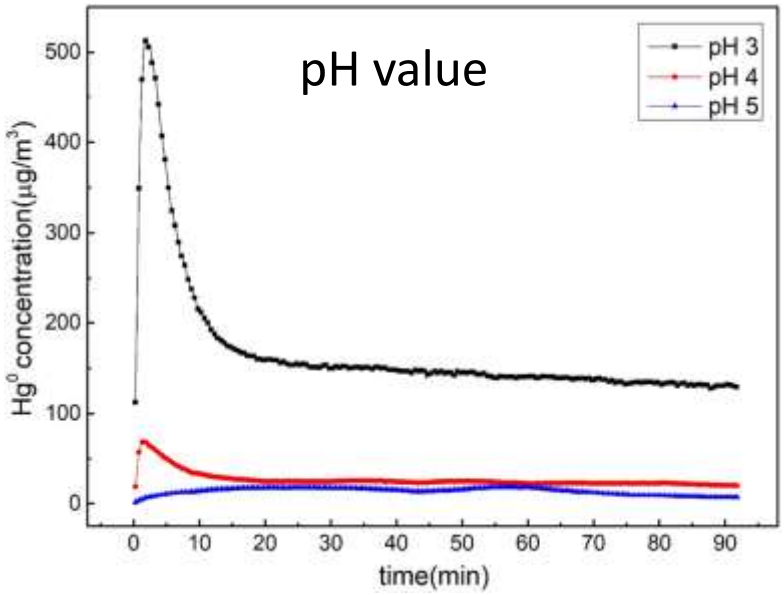


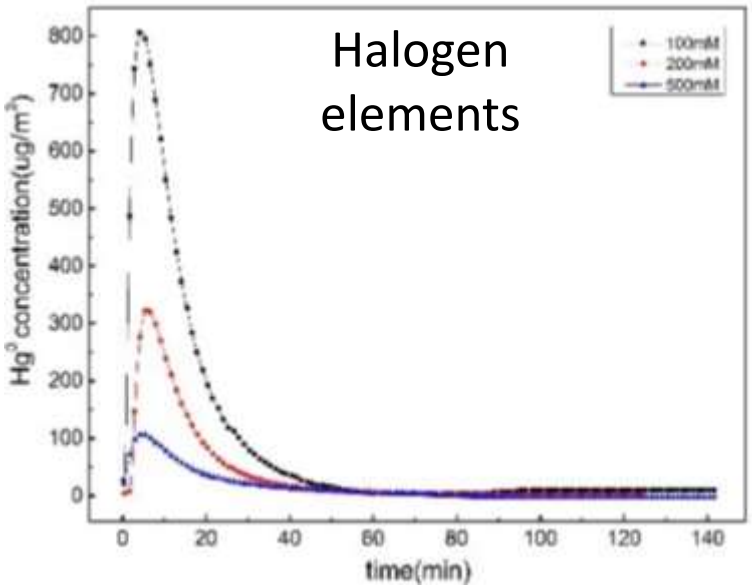


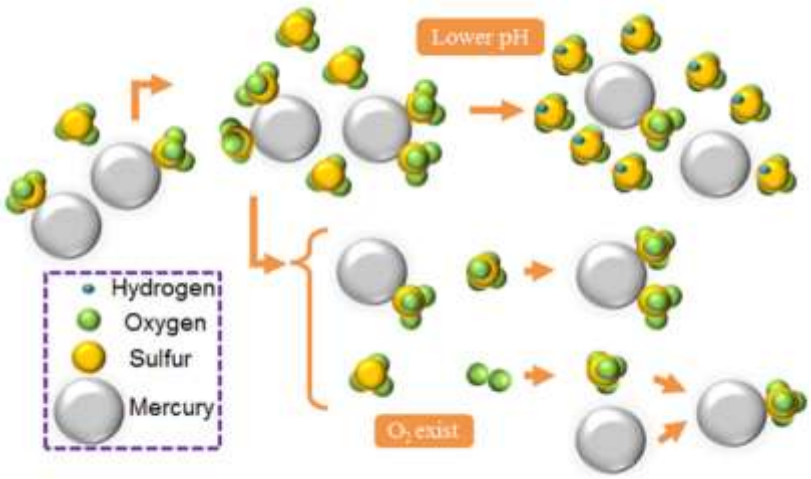


- The presence of SO_3^{2-} is responsible for Hg^{2+} reduction and re-emission in desulfurization slurry;
- Lower SO_3^{2-} concentration, higher reaction temperature, lower O_2 concentration lead to Hg^{2+} re-emission enhancement.

Hg re-emission in desulfurization slurry



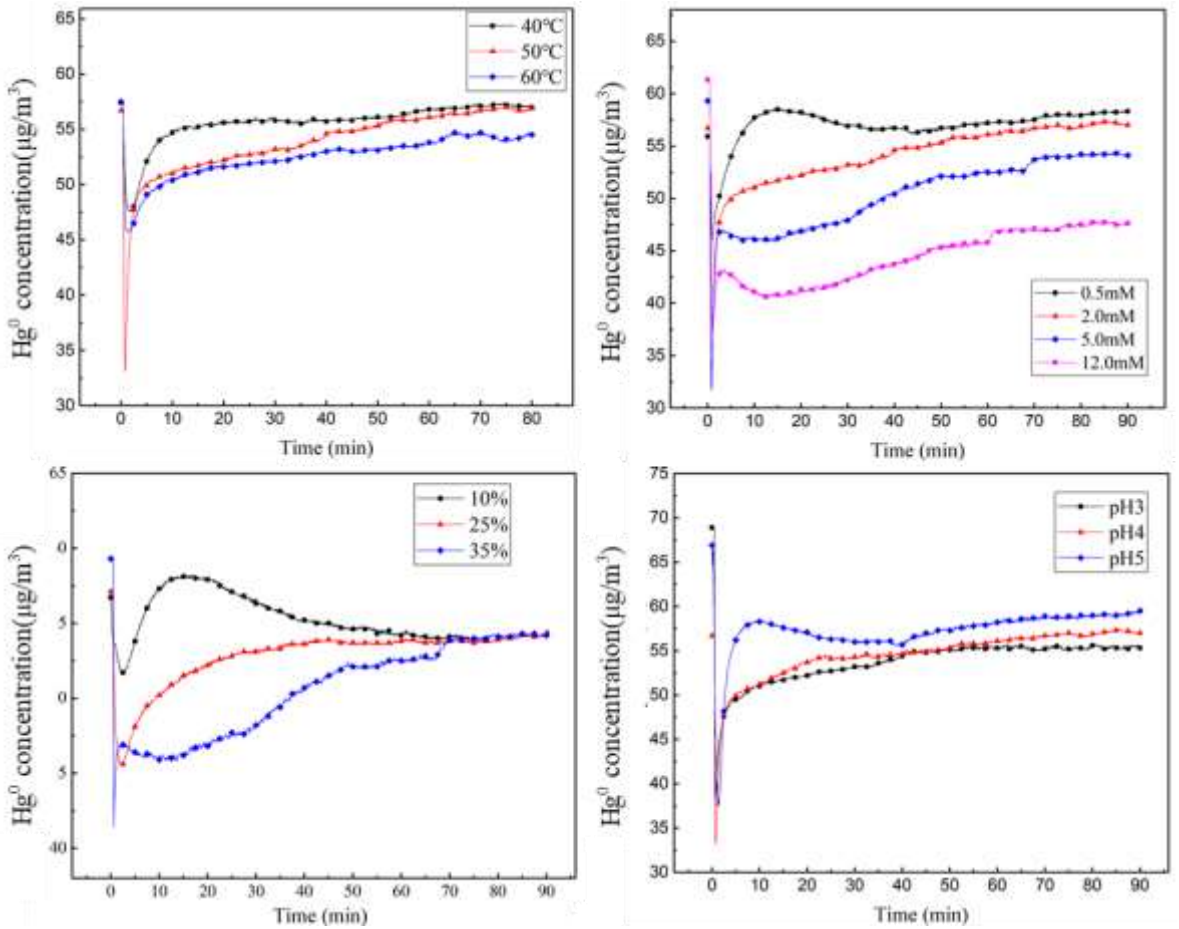




Hg re-emission mechanism

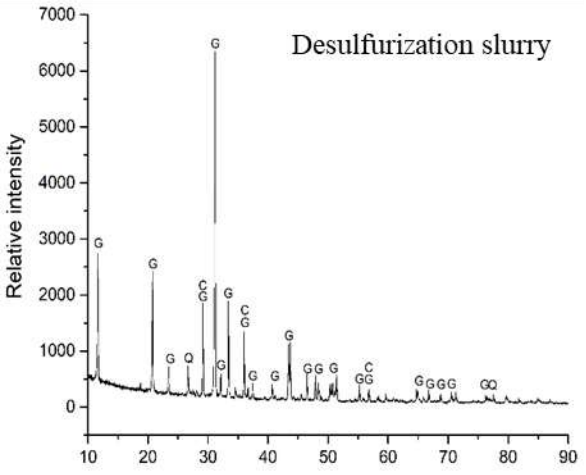
- An increase in pH inhibits Hg re-emission. Cl^- contributes to Hg^{2+} retention strongly.
- In WFGD system, abundant sulfite and chloride in desulfurization slurry, higher concentration of O_2 is positive for Hg re-emission inhibition.

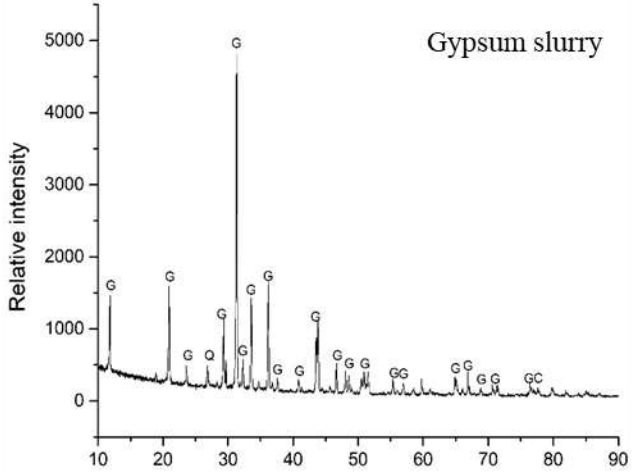
Hg re-emission in desulfurization slurry

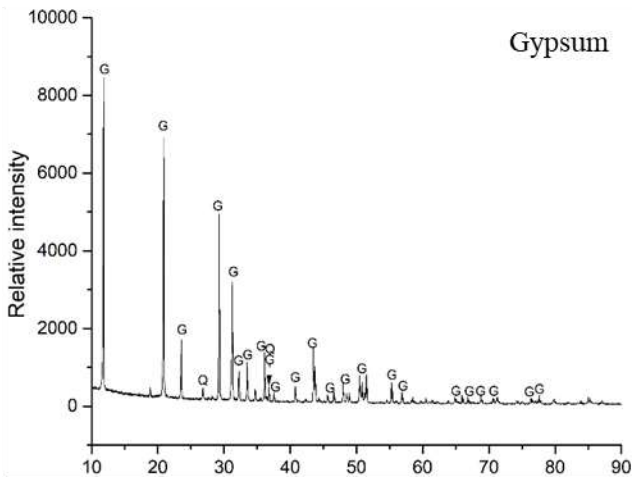


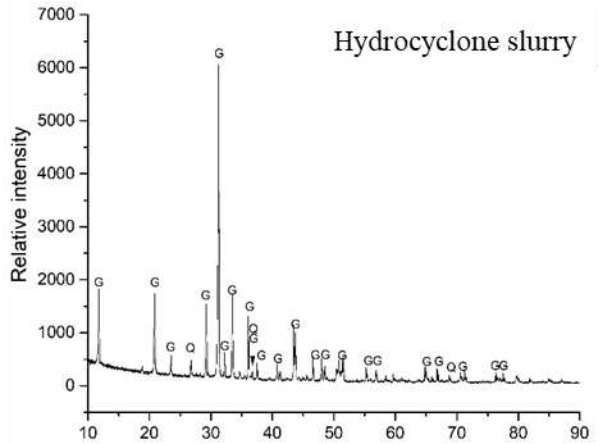
- $S_2O_8^{2-}$ promotes the conversion of Hg^0 to Hg^{2+}, which contributes to the stabilization of Hg in WFGD system;
- Increasing reaction temperature, $S_2O_8^{2-}$ concentration, and O_2 concentration, and decreasing pH value can enhance Hg^0 oxidation.

XRD results of gypsum production









C—Calcite；G—Gypsum；Q—Quartz

- The XRD results indicate that high proportion of gypsum and little quartz are found in the gypsum production process （ solid fraction of desulfurization slurry, gypsum slurry, gypsum hydrocyclone slurry, and gypsum）.
- In gypsum slurry, little calcite is found which indicates an uncompleted reaction of desulfurization agent.

Semi-quantitative XRD analysis

Semi-quantitative XRD result of solid fraction in gypsum production

	Calcite	Calcium sulfite	Quartz	Gypsum
Desulfurization slurry	13	8	6	73
Gypsum slurry	7	3	6	84
Gypsum	6	—	3	94
Gypsum hydrocyclone slurry	7	—	2	91

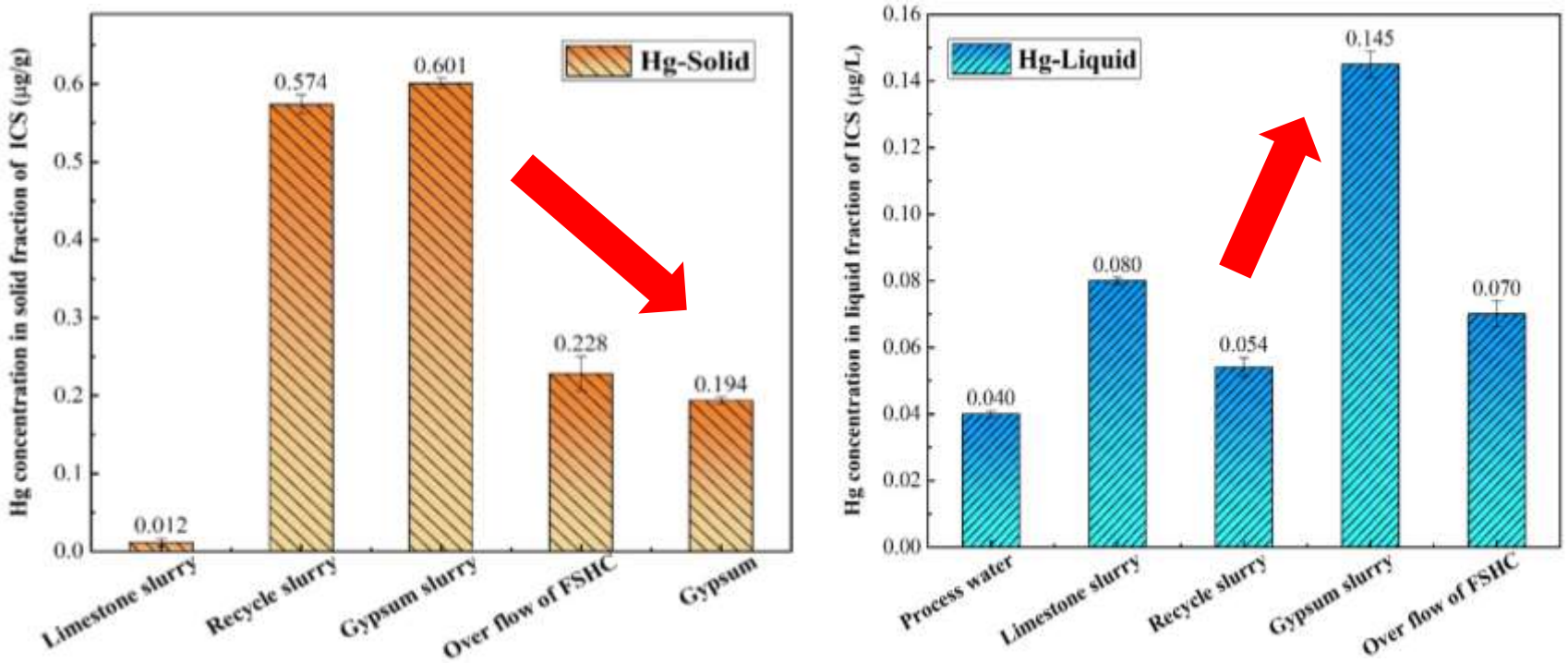
Gypsum production process:

$$CaCO_3 + SO_2 \rightarrow CaSO_3$$

$$CaSO_3 + O_2 \rightarrow CaSO_4$$

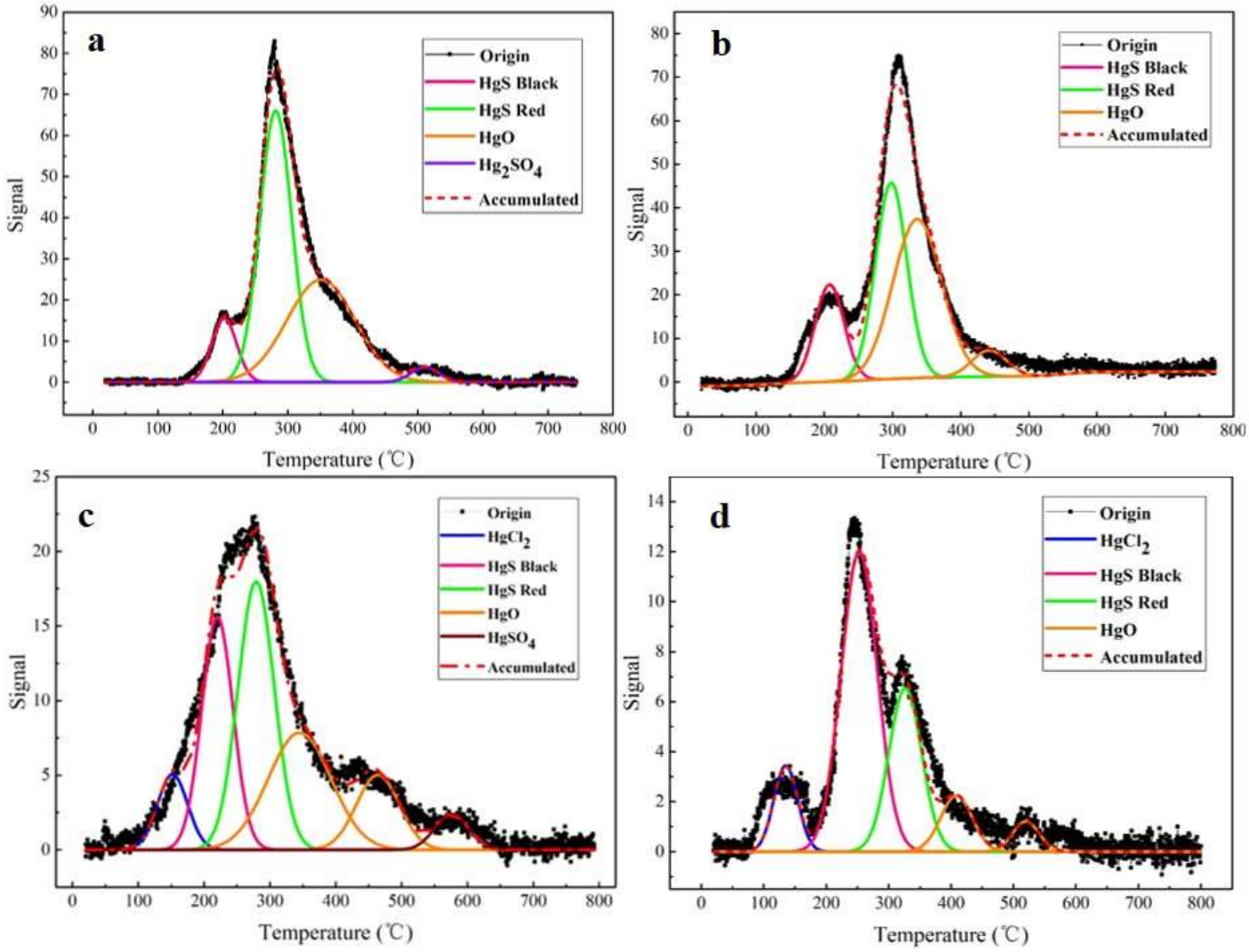
- The proportion of $CaSO_4$ in gypsum reaches 94% and the presence of little calcite and quartz may result from the capture of the fly ash in flue gas

Hg partitioning in gypsum production



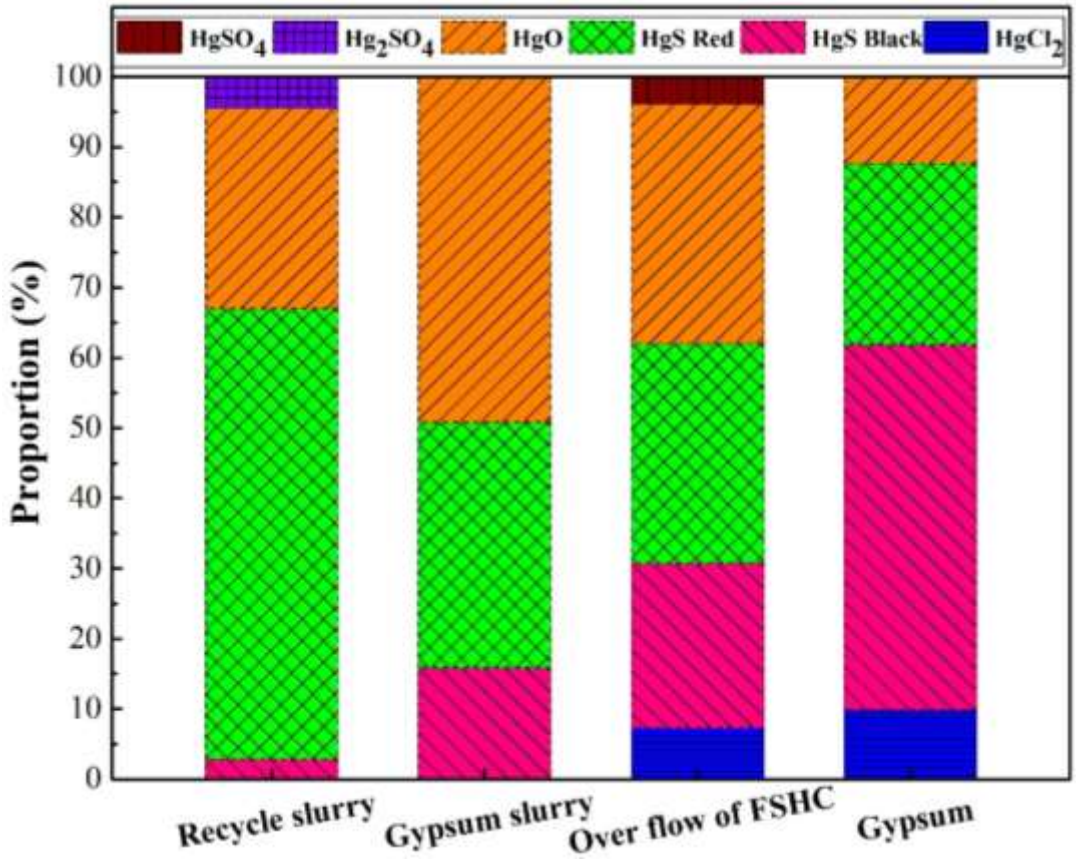
- Hg^{2+} in flue gas is washed off by desulfurization slurry which leads to an increase in Hg concentration from 0.054μg/L to 0.145μg/L in liquid fraction of gypsum slurry.
- The recycle of desulfurization solution resulted in Hg concentration increase in solid fraction of slurry.

Hg species in gypsum production



Identification of Hg species in gypsum production: a. desulfurization slurry; b. gypsum slurry; c. gypsum hydrocyclone slurry; d. gypsum

Hg species in gypsum production

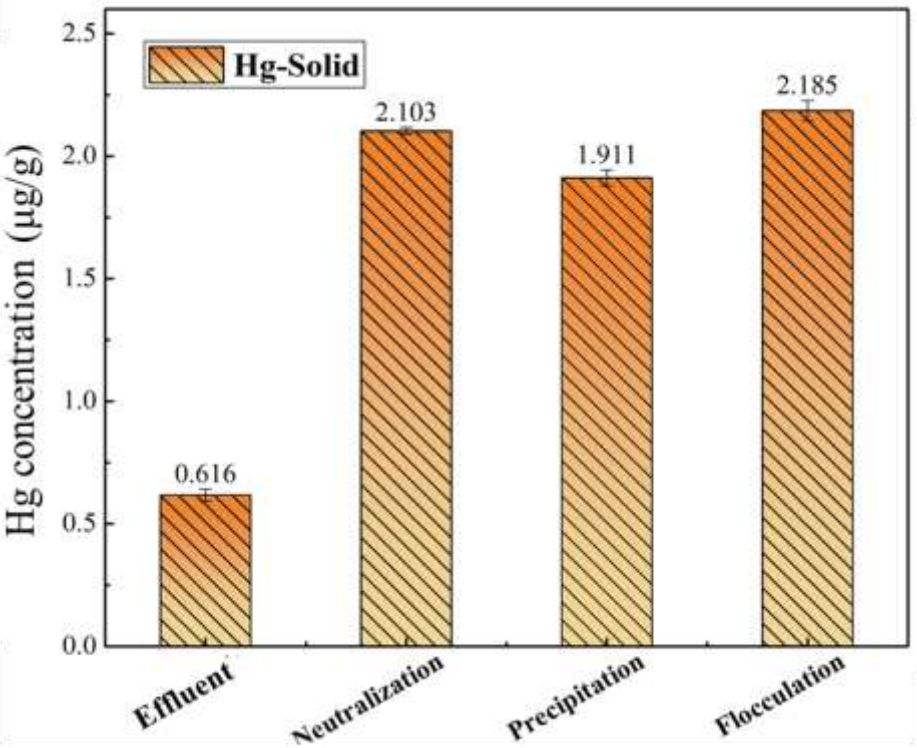


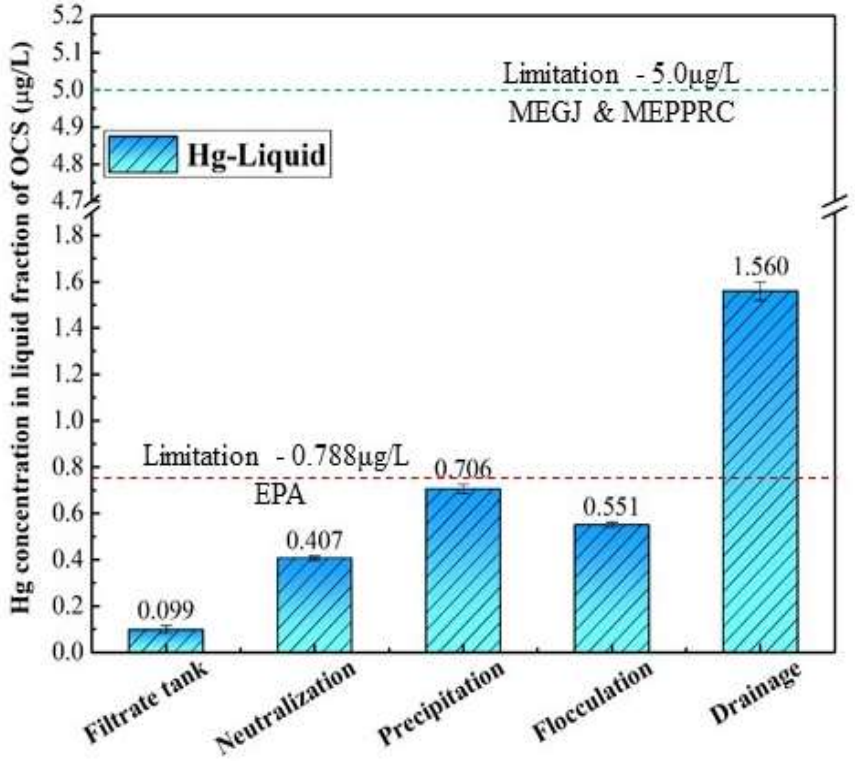
$4SO_3^{2-} \rightarrow 3SO_4^{2-} + S^{2-}$

$Hg^{2+} + S^{2-} \rightarrow HgS$

- The Hg species in gypsum production comprises $HgCl_2$, HgS(Black), HgS(Red), HgO, Hg_2SO_4, and $HgSO_4$
- The acidic environment in desulfurization tower promotes HgS production which increases Hg concentration in solid fraction.
- The proportion of HgS in desulfurization slurry, gypsum slurry, gypsum hydrocyclone slurry, and gypsum are 67.0%, 50.9%, 54.7%, and 77.8%, respectively.

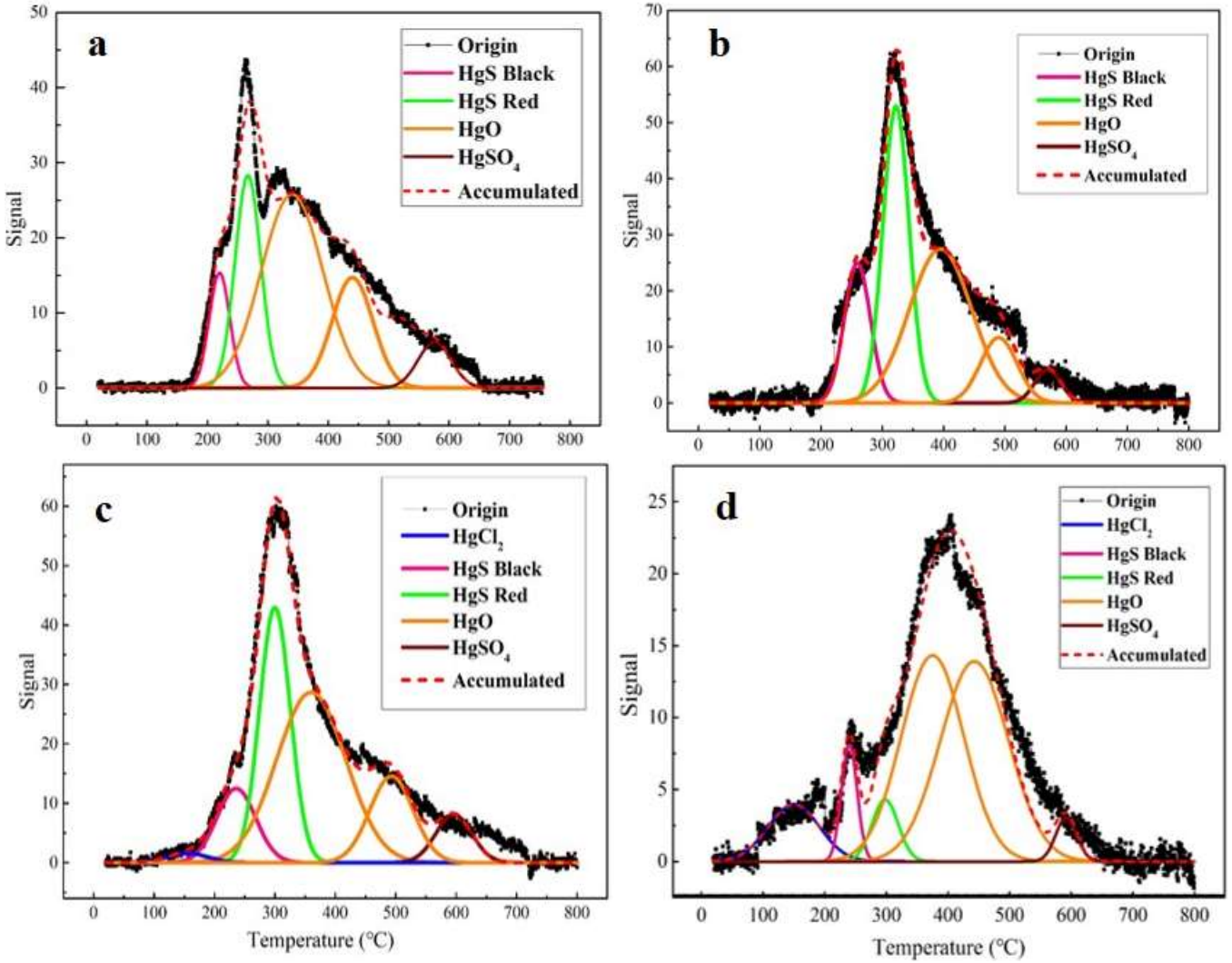
Hg partitioning in effluent treatment





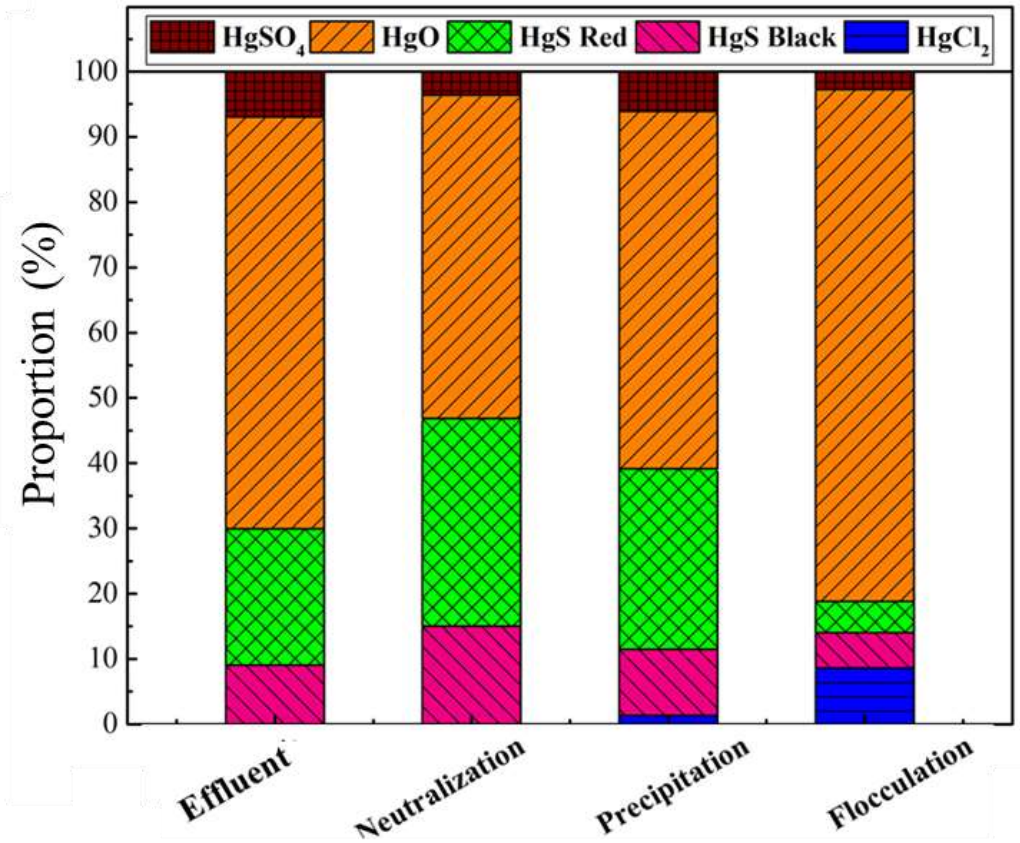
- The concentrations of Hg in the solid fraction and liquid fraction of effluent treatment process are higher than that of gypsum production process;
- Much attention need focus considering Hg concentration increases in liquid fraction, especially Hg concentration in the drainage is higher than corresponding emission limitation of EPA.

Hg species in effluent treatment



Identification of Hg species in effluent treatment: a. effluent ; b. neutralization tank; c. precipitation tank; d. flocculation tank

Hg species in effluent treatment



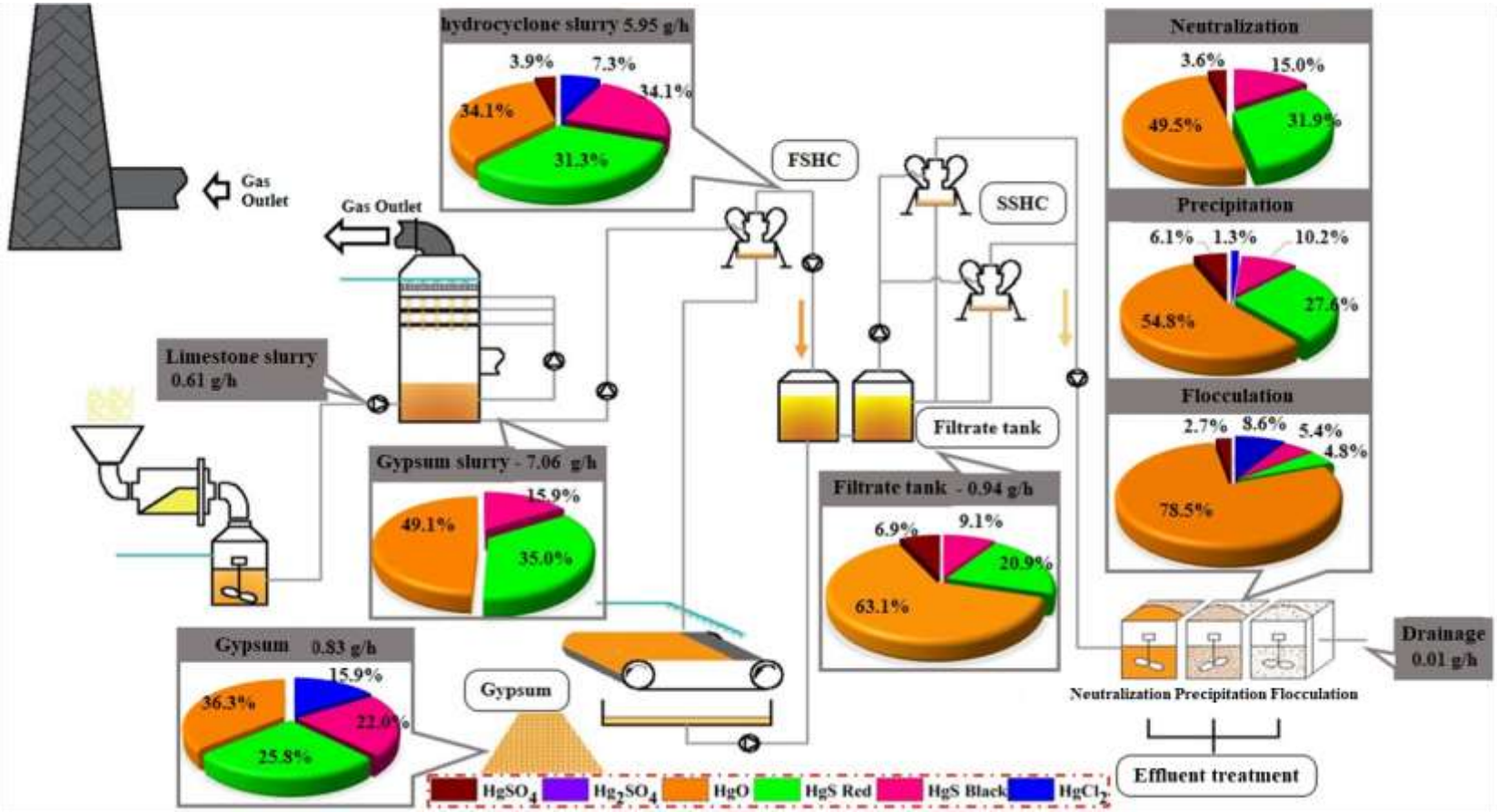
- The Hg species in effluent treatment comprises $HgCl_2$, HgS (Black), HgS (Red), HgO, and $HgSO_4$
- The presence of $HgCl_2$ in the solid fraction attributes to Cl- addition and larger particles in the precipitation tank.

- HgO is predominant species in effluent treatment; the proportion of HgS decreases and the proportion of $HgSO_4$ shows no obvious difference. After pH adjustment, alkaline environment is positive for HgO formation in solid fraction.

$$Hg^{2+} + 2OH^- \rightarrow Hg(OH)_2$$

$$Hg(OH)_2 \rightarrow HgO + H_2O$$

Migration behavior of Hg in WFGD



- There is about 0.83 g/h Hg contained in gypsum (14t/yr for total coal-fired power plants in China).
- Effluent treatment process removes 98.94% of total Hg in the effluent.

Summary

- Hg^{2+} re-emission in WFGD system is affected by SO_3^{2-}, halogen, $S_2O_8^{2-}$, etc. Generally, it is possible to retention Hg re-emission by optimizing the operation parameters of WFGD or additive .

- About 98.94% of total Hg in effluent was removed after effluent treatment resulting in the concentration of Hg in drainage is higher than the corresponding emission limitation.

- And the potential leaching of Hg in the gypsum is also worthy of enough attention. Potential risk of Hg release from the gypsum and sludge should be paid attention when they are utilized in downstream industries.

Thank you for your attention!

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