

Speciation Change of Flocs During Electrocoagulation for Wet Flue Gas Desulfurization Wastewater

CHEN ZHOU^{1*}, YUNBO XUE², XIANGLIANG LIU¹, JIANWEI CHEN¹, YU PENG²,
WENYI TAN^{2*}

¹China Power Hua Chuang Electricity Technology Research Co., Ltd, Shanghai, P.R. China

²Nanjing Institute of Technology, Nanjing, P.R. China)

Abstract. Wastewater produced from wet flue gas desulfurization (WFGD) process contains large amounts of suspended solids (SS), heavy metals and salinity. Compared to traditional chemical coagulation, electrocoagulation (EC) technology is a novel technology to remove these pollutants with lower O&M costs and simplified facilities. In order to achieve better EC effects, the speciation change of flocs generated from two kinds of sacrificed electrodes (e.g., Al and Fe) is investigated in various operation parameters. The results show that iron anode performed better compared to aluminium anode. At 20V of voltage and 6cm of electrode gap, the percentage of polymeric species of iron flocs can reach more than 50%. The significant domination of polymeric species under the optimal conditions during electrocoagulation is responsible for the turbidity removal.

Keywords: electrocoagulation, wet flue gas desulfurization wastewater, speciation, flocs, iron.

1.Introduction

In spite of various pollutants, such as SO₂, CO₂, NO_x, particles mass and toxic metals, produced from coal combustion, coal-fired power plants are still the main power source in worldwide. Many efforts have been made on the flue gas purification. Wet flue gas desulfurization (WFGD) is proved to be a practical technology in China, US, Japan, etc, due to its high efficiency and lower O&M costs. However, an amount of wastewater has to be discharged, in order to keep the limestone slurry as absorbent in reasonable ranges. The effluent from WFGD process contains complicated constitution, e.g., heavy metals, abundant Ca²⁺ or Mg²⁺ cations and SO₄²⁻, Cl⁻ anions, etc. Traditional technology to treat WFGD wastewater includes chemical precipitation method, through which only heavy metals and suspended solid (SS) can be removed in three sequent tanks, but most of salinity are still present. With stricter regulations in environment adopted, the demand in zero or near-zero liquid discharge increases invests sharply and novel technology to treat WFGD wastewater are in need.

Electrocoagulation (EC) becomes an attractive method for industrial wastewater treatment in recent decades. While the Al or Fe dissolves at anode and hydrogen gas is generated at cathode during electrocoagulation process, polymerized aluminum or polymerized ferrous flocculant is formed in-situ, which promotes polymerization of the pollutants particles. As a result, sedimentation, redox reactions and flotation occur in the same system, and EC is characterized by some advantages, such as high efficiency, fewer sludge products and no flocculants addition. These merits enable EC to be a promising treatment technology with respect to WFGD wastewater with complex constitution. Essentially, the EC process can be regarded as a combination of multiple physicochemical processes, and the critical process is the generation of flocculant. In case of Al anode, the dissolved Al³⁺ is present in form of hydrated cation Al(H₂O)₆³⁺, which immediately hydrolyzes in sequence into monomeric (or oligomer), polymeric and amorphous[1]. Different flocculants have different mechanisms for the removal of pollutants. The flocculant species through EC is heavily dependent on pH, Al³⁺ concentration, voltage, electrode gap, electrolyte composition, duration time and so on[2-4]. For example, when pH ≤ 6.5, Al³⁺ is present in form of hydrated cation Al(H₂O)₆³⁺ and of monomeric flocculant species with positive charge, e.g., Al(H₂O)₅(OH)²⁺, Al(H₂O)₄(OH)⁺, which are active for

*email: twy@njit.edu.cn; czhou@cpibj.com.cn

the removal of pollutants with negative charge. Instead of charge neutralization effects, Al^{3+} in form of amorphous $[\text{Al}(\text{OH})_3]_n$ exceeds 60 μmol and can remove pollutants by adsorption once $\text{pH} > 6.5$ [5]. To our best knowledge, few literature cover the speciation of flocs formed in WFGD wastewater and their role in remove some typical pollutants (e.g., SS, COD and heavy metals etc.) in WFGD wastewater. The emphasis of this study lies in the evolution of flocs speciation based on different sacrificed anodes and in the exploration of removal mechanism based on various flocs under operation conditions.

2. Materials and methods

An EC reactor was composed of a 3.5L cylindrical PMMA cell and two $15 \times 4 \text{ cm}^2$ parallel Al or Fe plates were immersed vertically into wastewater with an electrode gap of 2~6 cm. A DC power supply (RXN-305D, China) under constant voltage or current mode was connected to the plates. The details of experiment installation can be referred our previous paper.

Speciation determination

Ferron-complexation timed spectrophotometry method was employed to analyses Al or Fe species for WFGD wastewater flocs obtained from EC experiments under operation conditions. According to Parker and Bertsch's description, Al^{3+} reacts with Ferron complex reagent in different kinetic rates at $\text{pH}=5.2$ and $\lambda_{\text{max}}=370 \text{ nm}$ (Al). Three kinds of hydrolyzed Al species, monomeric species (Al_a), medium polymeric species (Al_b) and high polymers or colloidal species (Al_c) were identified quantitatively in line with reaction time, which is corresponding to that within 1 min, 1-120min and 120min. Herein, total aluminum concentration (Al_T) is the sum of Al_a , Al_b and Al_c . The fraction of Al_b can be regarded as a significant index in coagulation[6]. The detail of procedure includes the plot of stand curves and working curves.

Standard curves plotting. Take Al-Ferron curve as example, complex reagents including Ferron 8-hydroxy-7-iodo-5-quinoline sulfonic acid, 35% NaAc and 10% hydroxylamine HCl were prepared in advance and kept settling at 4-10°C for 4-5 days. An Al sheet with spectral purity was dissolved into hydrochloric acid and $C_{\text{Al}^{3+}}=0.1 \text{ mol L}^{-1}$ Al standard solution was calibrated. 0, 1, 2, 3, 4, 5 ml standard solution was added into 10ml Ferron complex reagents prepared, and measurements were performed on spectrophotometer(UV-3100, Shimazu). Al-Ferron standard curves were plotted on the dependence of absorbance on the Al concentration.

Fe-Ferron standard curves followed the same procedure, except that measurements performed at $\lambda_{\text{max}}=600 \text{ nm}$ (Fe). Afterwards, Fe-Ferron standard curves were plotted on the dependence of absorbance on the Fe concentration.

Working curves plotting. During WFGD EC process, 10ml samples were collected from 0 to 60 min at 10 min intervals, which were added into 10ml Ferron reagent and were diluted up to 100ml. The absorbance of each sample was immediately measured on spectrophotometer within less than 40s.

3. Results and discussions

Floc speciation change on Al anode

The dependence of Al speciation in EC process of WFGD wastewater on voltage and electrode gap is respectively shown in Figure 1 (a) and (b). Al_b content in WFGD wastewater is almost dominant in Al speciation distribution, but the domination over Al_a species is not obvious under some conditions. Al_b increases from 26% at 5V to 42% at 10V and then is stable with elevated voltage applied. The biggest Al_b content is obtained at 20V, at which turbidity removal can reach optimal value. On the other hand, Al_b content is dominant absolutely over other Al species at electrode gap of smaller than 4cm and decreases with the greater electrode gap. Different from the chemical coagulation, Al^{3+} is produced in-situ electrochemically when Al is used as anode. A series of hydrolysis products, including monomeric $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})^{2+}$ and dimeric $\text{Al}_2(\text{OH})_2^{4+}$ species, are generated in bulk solution. These hydrolysis products tend to interact with $\text{Al}(\text{OH})_4^-$ at the metal-solution interface, which is caused by water electrolysis reaction taking place on cathode, to form Al_{13} polymer[7-8]. Hu

and Mbacké et al proved that Al_{13} content in chemical coagulation process is positively correlated with turbidity removal and Al_b species is present in form of Al_{13} species[9-10]. The dependence of Al speciation in WFGD wastewater on electrode gap further prove that Al_b species can be regarded as an indicator of Al_{13} species in EC process, and Al_b domination in greater electrode gap range is attributed to high salinity in WFGD wastewater. Consequently the high conductivity of WFGD wastewater offsets the difficulty of longer diffuse distance and enables the electrogenerated Al^{3+} to meet hydroxyl and to form $Al(OH)_4^-$ as a precursor in such longer distance. However, the indicator of Al_b is not obvious in the dependence of Al speciation in EC process of WFGD wastewater on voltage. The comparable Al_a content to Al_b content is probably associated with the passivation of cathode in WFGD wastewater. With elevated voltages, excessive OH^- generated at cathode not only reacts with Al^{3+} , but also with abundant Ca^{2+} or Mg^{2+} in WFGD wastewater. As a result, insoluble $CaCO_3$ is produced in presence of CO_2 , which adsorbs onto the cathode and hinders the electrochemical reactions[11].

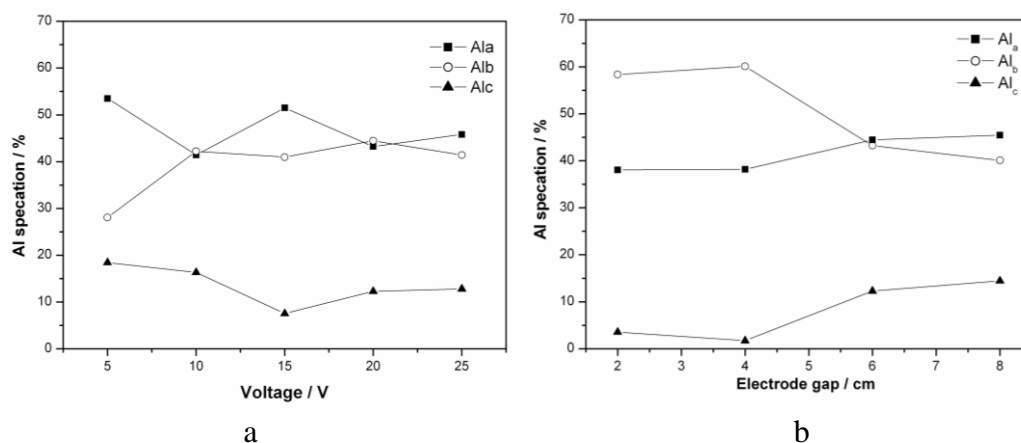


Figure 1. Al speciation in EC process of WFGD wastewater on voltage (a) and electrode gap (b)

Floc speciation change on Fe anode

In parallel to Al anode, the dependence of Fe speciation in EC process of WFGD wastewater on voltage and electrode gap is respectively shown in Figure 2 (a) and (b). The content of Fe_a and Fe_b basically dominate in the Fe species during EC process. With increased voltage, Fe_a content decreases while Fe_b content increases and both of them provide a stable content at around 45%. Fe_c content changes little at around 10%. It indicates that the transformation of Fe species influenced by voltages takes place only between Fe_a and Fe_b and no speciation change of Fe_c is observed. The content variations of Fe species with electrode gap is shown in Figure 2 (b), where the content of Fe_a and Fe_b still dominate in the Fe species during EC process. However, the content difference of Fe_a and Fe_b becomes more distinct at smaller electrode gap. With greater electrode gap, little change in Fe_a content and an increase in Fe_b content are observed, whereas Fe_c content decreases. The electrode gap has a more significant effect on the transformation of Fe_b and Fe_c than it does on Fe_a . According to the difference of reaction rate for various ferric hydrolysates with Ferron reagent, Fe_a represents ferric ions, monomeric hydroxy complex and ferric oligomer (e.g., Fe^{3+} , $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$), and Fe_b is a transition state between Fe_a and Fe_c , which is composed of polymeric hydroxy complex with low polymerization degree (e.g., $[Fe_2(OH)_2]^{4+}$, $[Fe_{13}(OH)_{34}]^{5+}$). Fe_c corresponds to the ferric species with high polymerization degree and even ferric precipitation (e.g., $Fe(OH)_3$ (am)) [12]. During the EC process of WFGD wastewater on Fe anode, the species of ferric hydrolysates dominate in form of low or medium polymerization state. Increased voltage favors the transformation from Fe_a to Fe_c , and as a result, polymerization degree of ferric species is enhanced slightly. On the other hand, greater electrode gap has an adverse effect on the formation of ferric high polymer. Associated with our previous works, it is also found that Fe_b content is positively correlated with turbidity removal.

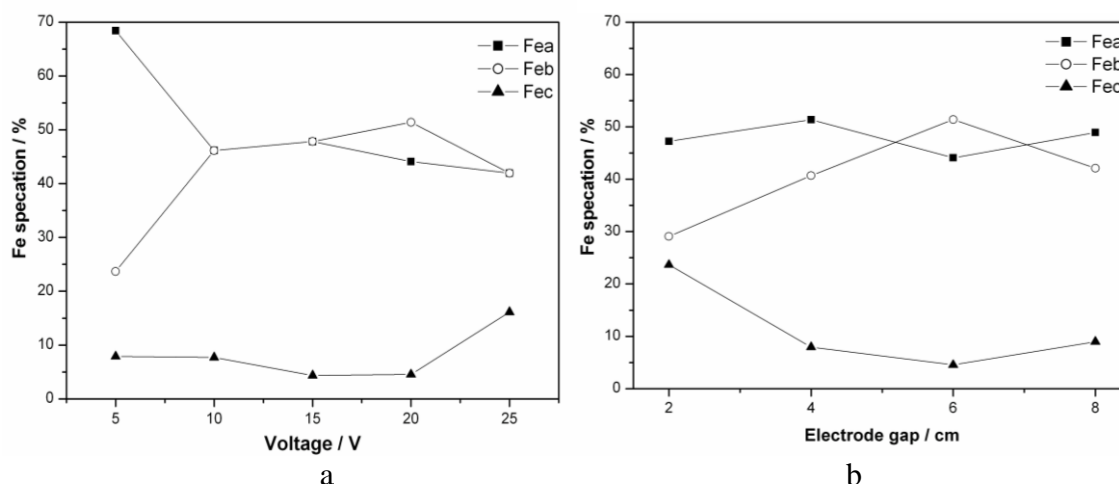


Figure 2. Fe speciation in EC process of WFGD wastewater on voltage (a) and electrode gap (b)

Floc speciation dependent on initial pH

As the dissolution of Al or Fe electrodes and the chemical form of corresponding ions are extremely dependent on pH atmosphere, the metallic speciation are compared in the range of initial pH ($pH_i=7\sim10$) as Figure 3 shows. There are respective optimal pH_i values for Al or Fe anode, and generally an alkaline atmosphere favors the formation of Al_b or Fe_b . Al_b reaches the max values at $pH_i=8$, while the max value for Fe_b occurs at $pH_i=9$. The Al speciation change differs from what Hu et al discovered before [8]. In our study, Al_c does not increase with higher pH_i condition. The profile of pH vs. time for WFGD wastewater during EC process is given in Figure 4. A decline, not an increase in pH with time is observed and then stable at a certain value. It indicates that the amount of hydroxyl ions available to the process of Al^{3+} hydrolysis-polymerization-gelation-precipitation becomes insufficient. When comparing Al anode with Fe anode, a lower pH value is obtained for Al anode. Fig. 5 also compares the evolution of Al_b and Fe_b speciation at same initial pH ($pH_i=9$). Both of their contents approach 45% after 10min. Fe_b content exceeds over Al_b content after 25min, and even increases gradually. It may be explained by the oxidation of ferrous cations, when dissolved oxygen (DO) is present.

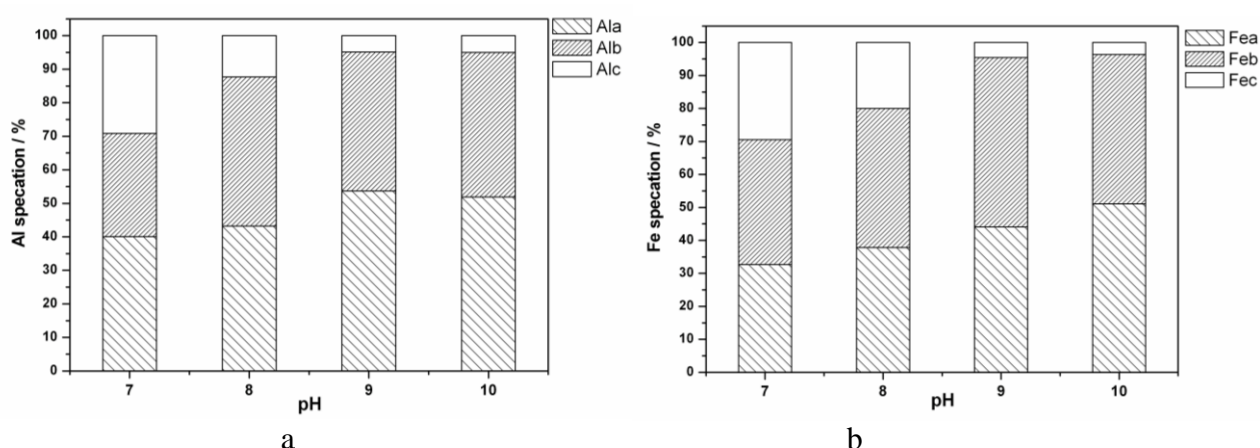


Figure 3. Distribution of Al(a) and Fe(b) speciation at different initial pH atmosphere

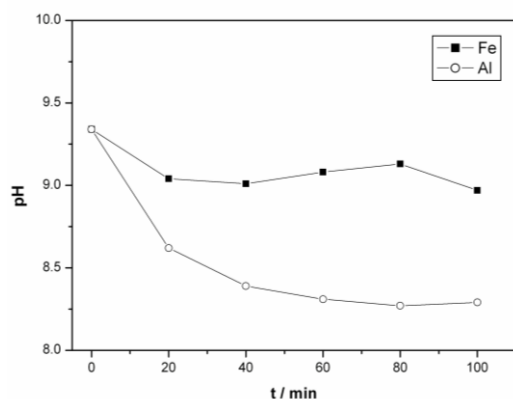


Figure 4. Evolution profiles of pH during EC process

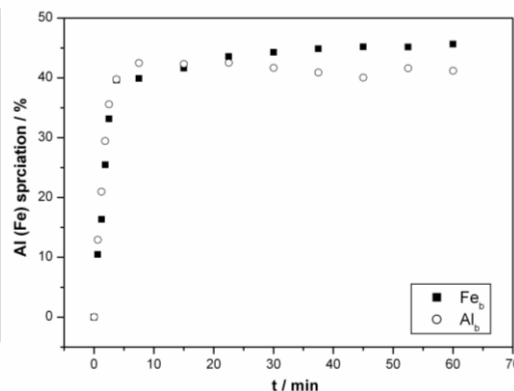


Figure 5. Evolution profiles of Al(b) or Fe(b) during EC process

4. Conclusions

Al and Fe flocs produced from electrocoagulation process for WFGD wastewater are investigated, in order to further discover the mechanism of pollutants removal. During electrocoagulation process, both of Al and Fe present speciation distribution, including Al(a), Al(b), Al(c) and Fe(a), Fe(b), Fe(c), respectively. Al(b) and Fe(b) respectively represent the generation of the polymeric hydroxy complex, when Al and Fe were used as anode during EC process. The higher contents of Al(b) and Fe(b) in speciation distribution favour the pollutant removal, but pH, voltage and electrode gap have impact on their generation as well as contents.

Acknowledgments. The authors acknowledge financial support from the National Natural Science Foundation (No. 51678291) and a Research Project of State Power Investment Company, China (No. 2017-010-ZDG-KJ-X). Dr Tan also appreciate the Jiangsu (China) - Finland Industrial R&D Program (No. BZ2018015) .

References

1. G. MOUEDHEN, M. FEKI, M. D. P. WERY and H. F. AYEDI, Behavior of aluminum electrodes in electrocoagulation process, *Journal of Hazardous Materials*, 150 (2008) 124
2. S. Y. LEE and G. A. GAGNON, Growth and structure of flocs following electrocoagulation, *Separation and Purification Technology*, 163 (2016) 162
3. S. Y. LEE and G. A. GAGNON, Comparing the growth and structure of flocs from electrocoagulation and chemical coagulation, *Journal of Water Process Engineering*, 10 (2016) 20
4. C. HU, J. SUN, S. WANG, R. LIU, H. LIU and J. QU, Enhanced efficiency in HA removal by electrocoagulation through optimizing flocs properties: Role of current density and pH, *Separation and Purification Technology*, 175 (2017) 248
5. J. DUAN and J. GREGORY, Coagulation by hydrolysing metal salts, *Advances in Colloid and Interface Science*, 100-102 (2003) 475
6. C. M. VAN GENUCHTEN, K. N. DALBY, M. CECCATO, S. L. S. STIPP and K. DIDERIKSEN, Factors affecting the Faradaic efficiency of Fe(0) electrocoagulation, *Journal of Environmental Chemical Engineering*, 5 (2017) 4958
7. W. ZHOU, B. GAO, Q. YUE, L. LIU and Y. WANG, Al-Ferron kinetics and quantitative calculation of Al(III) species in polyaluminum chloride coagulants, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 278 (2006) 235
8. M. G. KILİ and Ç. HOŞTEN, A comparative study of electrocoagulation and coagulation of aqueous suspensions of kaolinite powders, *Journal of Hazardous Materials*, 176 (2010) 735
9. C. HU, S. WANG, J. SUN, H. LIU and J. QU, An effective method for improving electrocoagulation process: Optimization of Al13 polymer formation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 278 (2006) 235



Engineering Aspects, 489 (2016) 234

10. M. K. MBACK , C. KANE, N. O. DIALLO, C. M. DIOP, F. CHAUVET, M. COMTAT and T. TZEDAKIS, Electrocoagulation process applied on pollutants treatment- experimental optimization and fundamental investigation of the crystal violet dye removal, Journal of Environmental Chemical Engineering, 4 (2016) 4001

11. C. HU, H. LIU, J. QU, D. WANG and J. RU, Coagulation Behavior of Aluminum Salts in Eutrophic Water: Significance of Al¹³ Species and pH Control, Environmental Science & Technology, 40 (2006) 325

12. C. M. VAN GENUCHTEN, S. R. S. BANDARU, E. SUROROVA, S. E. AMROSE, A. J. GADGIL and J. PE A, Formation of macroscopic surface layers on Fe(0) electrocoagulation electrodes during an extended field trial of arsenic treatment, Chemosphere, 153 (2016) 270

13. H. L. ZHENG, X. H. HUANG, Q. HE and D. D. LI, Study of ferric species distribution in polyferric silicate sulfate (PFSS) prepared from tetraethylorthosilicate (TEOS), Spectroscopy and Spectral Analysis, 28 (2008) 543

Manuscript received: 10.02.2020