CHEMICAL ENGINEERING TRANSACTIONS

VOL. 46, 2015

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Peiyu Ren, Yancang Li, Huiping Song

ISBN 978-88-95608-37-2; **ISSN** 2283-9216

DOI: 10.3303/CET1546189

Study on Processing Desulfurization Waste Water of Power Plant Using Polymeric Flocculant

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The power plant desulfurization wastewater is studied in a city of North China. The optimal conditions for preparing polymeric polysilicate aluminium ferric sulphate (PSAFS) was explored by $L_9(3^4)$ Results of Orthogonal Experiment, and the effect of dosage, pH value, the settling time and sedimentation time on PSAFS for disposal was investigated as well. It was shown that the performance of PSAFS was the best, while the concentration of SiO_2 was 2.5%, the value of pH was 5.5, and the molar ratio of Al/Fe/Si was 1:1:1, aging time about 4 h. Under the conditions of PSAFS dosage 6.7 g/l and wastewater pH 10, settling time of 20 min, the suspended solids, COD, sulfide, fluoride and Cl^- in the desulfurization wastewater had a good removal effect. Comparing with the polyaluminium chloride (PAC) for the treatment of the desulfurization waste water, PSAFS has the advantages such as less dosage, the higher efficiency, shorter settling time and co- treatment many pollutants.

1. Introduction

With the increasing air pollution, entering atmospheric nitride and sulfide was strict control in china. NO_x and SO_2 were processed in Power enterprises because of emissions.

Most thermal power plants adopt wet limestone-gypsum flue gas desulfurization (FGD) in power generation, during which process the desulfurization waste water is produced by the gypsum dehydration system (Cui Li and Chen Yingmin (2008)).Impurities in desulfurization waste water mainly come from flue gas, desulfurizer and producing water. Among them, polluting components mainly come from flue gas, and the impurities in flue gas are primarily from coal burning. Coal contains various elements, including heavy metals. Compounds are formed from these elements after burning, among which gaseous compounds go to desulfurization system along with flue gas and then solubilize in absorbency slurry. The features of the desulfurization waste water produced in this process are mainly (Zhou Weiqing and Li Jin (2006)): (1) PH value is relatively low and the water appears acid; (2) A great amount of suspended solids and metallic ions are contained; (3) Trace amount of heavy metallic ions are contained; (4) There are many anions such as F^-, SO_4^{2-}, Cl^-.

As a widely used water treatment agent, polymeric flocculant is the key and core basis of flocculating water treatment technology and is now applied broadly to desulfurization waste water treatment in power plant [4]. But the application of polymeric flocculant can be influenced by many factors, including flocculant's physiochemical properties, the distribution law of flocculating activity, flocculation mechanism, and the environment of desulfurization waste water, etc [5]. A case study of polyaluminium chloride (PAC), Polymeric Aluminum had some disadvantages such as high toxicity, long settling time and low efficiency; And Polymeric Ferrite easy to make water yellow. (Tang Hongxiao (2006)). Combined with the advantages of Polymeric Aluminum and Polymeric Ferrite Flocculants, a high polymeric flocculant was synthesized, which is named polysilicate aluminium ferric sulphate (PSAFS). PSAFS has the advantages such as less dosage, the higher efficiency, shorter settling time and co- treatment many pollutants. (Tang Xiaodong et al (2015))

Please cite this article as: Zhang J.H., Liu J.L., 2015, Study on processing desulfurization waste water of power plant using polymeric flocculant, Chemical Engineering Transactions, 46, 1129-1134 DOI:10.3303/CET1546189

2. Mensuration of water sample

Water sample for experiment was collected from a power plant in a city of North China. The Power Plant adopts wet limestone-gypsum flue gas desulfurization (FGD). The qualities of waste water produced there are shown in table 1:
Materials whose content in the waste water exceeded the standard considerably include suspended solids, sulfide, and other materials whose content in the waste water exceeded the standard include COD and fluorides. The experiment designed in this paper is aimed to remove suspended solids (SS), COD, sulfide and fluorides.

Table 1: Qualities of Waste Water Produced in Power Plant

Pollutants	Results	How the Results Meet the Standard
PH	6.43	reached the national grade 1
suspended solids(SS)	2074	exceeded the standard considerably
turbidity	896	----
COD	195.5	exceeded the national grade 2
sulfide	6.6685	exceeded the standard considerably
sulphate	1714.72	met the standard
fluoride ion	15	exceeded the standard
chloride ion	1214.6	-----

3. The preparation of flocculant

(1) Method of preparing flocculant
At room temperature, certain amount of sodium silicate was weighed and dissolved in water and then the solution's pH was regulated to about 5.5 using 20% sulfuric acid and 1.0 mol/L NaOH. After activation for some time, 0.5 mol/L aluminium sulfate and 0.5 mol/L ferric sulfate were added according to scheduled proportion under intense mixing which sustained for 10 min. Finally, the solution was diluted to certain concentration with water and then aged in still standing (Yang Daigui et al (2005)).
(2) Conditions of Preparing Flocculant
Reaction rate of hydrated silica's polymerization is primarily influenced by factors such as temperature, acidity, mass concentration of SiO_2, co-existing ions, etc. Among them, the most influential one is the pH value of sodium silicate solution. Dilute sulfuric acid was used to regulate sodium silicate's pH. The time differences of sodium silicate solution appearing from light blue to gel under different pH and SiO_2 mass concentration were recorded in table 2 and table 3.

Table 2: Hydrated Silica's Polymerization under Different pH (at Room Temperature, SiO_2 Mass Concentration at 2.5%)

PH	3.0	4.3	5.4	5.8	6.6
T (min)	—	200	10	8	1

Table 3: Hydrated Silica's Polymerization under Different SiO_2 Mass Concentration (at Room Temperature, pH at 5.5)

SiO_2%	1.5	2.0	2.5	3.0	3.5
T (min)	20	16	10	1.5	0.5

Keep pH and polymerizing time of activating hydrated silica under control and find the best timing for introducing metallic ions. Introducing metallic ions during appropriate time can not only help to control hydrated silica's polymerization degree but also enable ferric-silicon aluminum's copolymerization, and thus reach the best combination of products' abilities of charge neutralization and adsorption bridging.
(3) Orthogonal Experiment (Writing Group of Orthogonal (1976))
In order to compare flocculant prepared under different conditions in orthogonal experiment, this paper carried out waste water treatment experiment using desulfurization waste water of second stage from the Power Plant and proceeded the comparison through measuring the turbidity of water after treatments.

Preliminarily, take 150 ml waste water and 1.0 g PSAFS. Maintain pH at 10 and stirring speed at 100r/min. After 20 minutes of stirring and another 20 minutes of still standing, take the supernatant liquor to measure the turbidity for comparison.

Table 4: $L_9(3^4)$ Table of the Orthogonal Experiment

Factor Levels	Al/Fe	(Al+Fe)/Si	Aging Time
1	4: 6	2: 1	2h
2	5: 5	1: 1	4h
3	6: 4	1: 2	6h

Results of Orthogonal Experiment selected according to factor criterion mentioned in table 4 are shown in table 5:

Table 5: $L_9(3^4)$ Results of Orthogonal Experiment

Factor Levels	1	2	3	4	5	6	7	8	9	Mean Value 1	Mean Value 2	Mean Value 3	Differential
A	4:6	4:6	4:6	5:5	5:5	5:5	6:4	6:4	6:4	82	74	89	15
B	2:1	1:1	1:2	2:1	1:1	1:2	2:1	1:1	1:2	72	84	89	17
C	2	4	6	2	6	4	6	2	4	80	76	89	13
D	23	23	36	24	28	22	25	33	31				

Note: A —Al/Fe; B—Al+Fe/Si; C—Aging time; D—turbidity

The result in table 5 that 17>15>13 implies that the influential power of different factors should be permuted as Al+Fe/Si>Al/Fe>aging time.

From Table 5 it can be seen that:

Among the three factors, proportion of Al/Fe plays an important role. Proportion of Al/Fe directly influences flocculant’s property. Along with the increase of Al/Fe proportion, the flocculating performance gets higher and then becomes lower, with a peak. When the Al/Fe proportion is 1:1, waste water treatment achieves best results, with the lowest level of turbidity, which at the same time suggests that only when the contents of aluminum and ferric are at the same level can the advantages of PSAFS be shown because the proportion can give full play of aluminum and ferric flocculants’ strengths and weaken the two’s shortcomings so as to achieve the treatment’s best performance. (LIU Zhian (2011))

Among the three factors, proportion of Al+Fe/Si plays the biggest part. In polysilicate aluminum ferric sulfate, Si is anion, negatively charged, while Al or Fe is cation, positively charged. Polysilicate and polymerization of Al and Fe can increase flocculant’s abilities of charge neutralization as well as adsorption bridging. (Zhang Qiong et al (2015)) The number of charges inpolysilicate aluminium ferric sulphate is also an important factor. With the proportion of Al+Fe/Si increasing, the flocculating performance begin with slight improvement and then sharp attenuation. When the proportion of Al+Fe/Si is 2:1, the treatment achieves best performance, with the lowest level of turbidity. At this time, Al and Fe can just be polymerized by hydrated silica and during the treatment will not increase Al’s or Fe’s content. (Wang Zhixuan and Zhao Huiming (2008))

In experiments under five levels of aging time, with aging time increasing, the flocculating performance gets better and then weaker, with a peak. Since during the preliminary stage of flocculant preparation, influenced by metallic ions, polymerizing rate of hydrated silica and the degree of polymerization are relatively low; also, molecular chain of polysilicate is short and flocculant’s abilities of bridging cementation and sedimentation sweeping are weak, which are shown during the coagulation by small alum grains and low rate of sedimentation. As the aging time extends, the degree of flocculation get higher, the length of molecular chain of polysilicate grows gradually, flocculant’s ability of sweep aggregation is strengthened, and the flocculating performance is improved, which are shown by big alum grains and high rate of sedimentation. (Zheng Dingcheng et al (2011)) But when the degree of polymerization of polysilica is heightened further, the chain structure of polysilica molecules is transited into net structure and finally becomes gel. Consequently, long chains’ ability of sweep aggregation is limited again and the alum grains get smaller. If Fe’s mass concentration is not big enough, the floc’s structure will be unconsolidated and thus the sedimentation rate gets lower and the flocculant performs in a weaker way. Besides, the larger Si’s mass concentration is, the less influences will be brought by metallic ions upon hydrated silica’s polymerization. As a result, hydrated silica will be polymerized more quickly and less time will be taken for the hydrated silica molecule to grow from small ones to longer chains and further from chains to forming net structure. So, the “best aging time” is achieved. When the aging time is 4 hours, there will be best flocculating performance and the lowest turbidity. Because the time span is two hours in these experiments, single factor tests will be carried out in the next step over aging time.

4. Treat desulfurization waste water with PSAFS

(1) Design of orthogonal experiment
Considering that factors influencing the effectiveness of the treatment include: (1) pH of waste water before adding reagent; (2) quantity of reagent; (3) stirring time (min); (4) time of still standing (min), three levels of each factor are chosen. Choose the orthogonal table $L_9(3^4)$ and take 150 ml waste water for treatment. Compare the turbidity of supernatant liquor of waste water after treatment.

Table 6: Orthogonal Experiment $L_9(3^4)$

Levels of Factors	pH	Quantity of Reagent (g)	Stirring Time (min)	Time of Still Standing (min)
1	8	1	10	10
2	9	2	20	20
3	10	3	30	30

Results of orthogonal experiment selected according to levels of factors in table 6 are shown in table 7:

Table 7: Results of Orthogonal Experiment $L_9(3^4)$

Factor Levels	1	2	3	4	5	6	7	8	9	Mean Value 1	Mean Value 2	Mean Value 3	Differential
pH	8	8	8	9	9	9	10	10	10	113	112	83	30
E	1	2	3	1	2	3	1	2	3	86	118	104	32
F	10	20	30	20	30	10	30	10	20	107	89	112	23
H	10	20	30	30	10	20	20	30	10	140	84	84	56
D	46	32	35	21	58	33	19	28	36				

Note: E—quantity of reagent; F—stirring time; H—time of still standing; D—turbidity

From table 7 it is clear that: 56>32>30>23, which suggests that the influential power of pH, quantity of reagent, stirring time and time of still standing are permutated as: time of still standing>quantity of reagent>pH>stirring time.

5. The determination of coagulant aid's quantity

Use different amounts of polyacrylamide (PAM) and prepared PSAFS to treat waste water and determine the optimum quantity of polyacrylamide (PAM).
Flocculate the waste water: take 5 sets of 150 ml waste water respectively and regulate the pH to 10. Add 1.0 g PSAFS and 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g PAM into each. After 20 minutes of stirring and another 20 minutes of still standing, measure the turbidity of supernatant liquor for comparison.

Table 8: Experiment Results under Different Amounts of PAM

Quantity of PAM (g)	Turbidity
0.1	8.2
0.2	5.4
0.3	4.7
0.4	5.5
0.5	6.8

It is found that when the quantity of PAM is 0.3 g, time for forming alum grains is shortened and the alum grains formed are bigger and thicker, with the lowest level of turbidity.

6. Results of flocculating treatment

Measure and pour 150 ml waste water into 200 ml beaker and regulate pH to 10. Add 1.0g PSAFS and 0.3 g polyacrylamide. After 20 minutes of stirring and another 20 minutes of still standing, analyze the water sample and the results are shown in table 9:

Table 9: Results of Flocculating Treatment

Order Number	Pollutant	Results
1	PH	8.3
2	suspended solids (ss)	65
3	turbidity	4.7
4	COD	92.43
5	sulfide	0.833
6	sulphate	1826.26
7	fluoride ion	0.4
8	chloride ion	597.8

Comparisons of results of waste water treatment between using PSAFS and widely used flocculant PAC in power plant are shown in table 10.

Table 10: Comparison of Treatment Efficiency between PSAFS and PAC

Order Number	Pollutant	Removal Rate of PSAFS	Removal Rate of PAC
1	PH	—	—
2	suspended solids	96.86%	94.02%
3	turbidity	99.47%	99.08%
4	COD	52.72%	46.11%
5	sulfide	87.50%	78.82%
6	fluoride ion	97.33%	84.00%
7	chloride ion	50.78%	30.25%

From the table above it can be seen that the treatment effectiveness of PSAFS apparently outweighs that of traditional flocculant PAC.

7. Conclusions

(1) Through orthogonal experiments it is determined that the best conditions for preparing PSAFS are: SiO_2's concentration at 2.5%, pH value at 5.5, proportion of Al/Fe/Si at 1:1:1 and the aging time at 4 hours;
(2) After treating water samples using the prepared PSAFS, through orthogonal experiments it is determined the optimum quantity of reagent and treatment environment are: pH value at around 10, stirring time at 20 minutes, time of still standing at 20 minutes and the quantity of reagent at 6.7 g/l water;
(3) Polyacrylamide was used as coagulant aid and the optimum process conditions are determined: the quantity of coagulant aid added is 1g/L, and pH value should be 10;
(4) Comparing with PAC for the treatment of the desulfurization waste water, PSAFS has the advantages such as less dosage, the higher efficiency, shorter settling time and co- treatment many pollutants. After

treatment, except suspended solids whose content reached the national second-grade standard of waste water discharge, contents of other pollutants in water samples all reached the national first-grade standard of waste water discharge.

Acknowledgments

This work was financially supported by the Fundamental Research Funds for the Central Universities 2014 MS125.

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