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Effect and mechanism of coking residual ammonia water treating by flue gas

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Abstract: The treatment of coking residual ammonia water has been a big difficult problem at home and abroad, and there is no breakthrough research achievement in the past. The invention patent "The method of treating all coking wastewater or treating coking residual ammonia water by flue gas" has been successfully used in Huaian Steel Works for high concentration and organic industry wastewater treatment. Not only can it realize the wastewater zero discharge, but also the wastewater treatment has an effect of de-sulfur and de-nitrogen for flue gas. So that the flue gas exhaust can meet the requirement of emission standard. The mass transfer and heat transfer, fly ash absorption and coagulation, acid and alkali neutralization reaction, catalysis oxidation and reduction reaction in flue gas would be the major factors.

Key words: flue gas; coking residual ammonia water; zero discharge; de-sulfur; de-nitrogen

Introduction

Coking wastewater, especially the coking residual ammonia water (a huge volume and heavy polluted wastewater in coking) is a high concentration organic industry wastewater of difficult for the biochemistry degradation. Of which, BOD_5/COD is usually about 30%. At present, by the treatment of extended (or intensified) aeration biochemical method which is generally adopted at home and abroad, the COD cannot meet the requirement of discharge standard and the color, offensive smell are also unbearable. The ammonia and nitrogen concentration are seriously exceed the discharge standard. The average concentration of ammonia nitrogen (NH_3-N) in China's metallurgical discharged wastewater is as high as 300 mg/L, which is 20 times higher than the first class discharge standard (15 mg/L) stipulated for coking wastewater polluter discharge of China's iron and steel industry.

The ammonia nitrogen in coking wastewater means that nitrogen exists in form of the free state NH_3 or NH_4. The free state NH_3 is very poisonous, especially for fish. Its lethal concentration for different species of fish is 0.2—2.0 mg/L (NH_3) (EPA, 1981). Ammonia nitrogen is also one of the factors to cause water body eutrophication. Besides, there are large quantities of organic nitrogen compound in the coking wastewater, such as pyridine, quinoline, indole, organic nitrile, organic amine and so on. Ammonium nitrite formed by the reaction of organic amine and nitrite has the effects of carcinogenesis and teratogenesis. Only in China's metallurgical industry, there are as many as 42000 tons of ammonia and nitrogen being discharged into the water every year.

Since the ammonia nitrogen, especially the organic nitrogen compounds seriously endanger human being and ecosystem. Therefore, de-nitrogen from coking wastewater is much concerned worldwide. There are various methods in nitrogen removing, such as bio-nitrify- and anti-nitrify method; reed soil treatment method; chemical precipitation method; chloride method; ion exchange method; active carbon absorption method; fly ash absorption method and so on. Except the bio-nitrify-anti-nitrify method. Most of other methods are used together with the genal biochemical method, which are used in the countries such as Poland, Japan, Germany and China. The bio-hitrify-anti-nitrify method had better denitrofication, which can remove not only the inorganic nitrogen, but also can remove the organic nitrogen. While the investment and operation cost is very expensive. In China, the A/O method used in Baoshan Iron and Steel Works is one of the bio-nitrify-anti-nitrify methods.

For coking wastewater treatment, the study focuses in finding out a method with less investment, lower operational cost and good treatment efficiency. The invention patent "The method of treating all coking wastewater or treating coking residual ammonia water by flue gas"(Cheng, 1999) has been successfully used in Huaian Steel Plant for the project of coking residual ammonia water treatment. Not only can it realize the pollutants' zero discharge in wastewater, but also the wastewater treatment has an effect of de-sulfur and de-nitrogen for flue gas, and the exhausted flue gas would meet the requirement of national emission standard. Since it is "treating the waste by waste", consequently, the method has the advantages of good treatment effect, less investment and lower operational cost.

1 Operational effect of coking residual ammonia water treatment project in Huai Steel Plant

The flue gas from two sets of 10 t/h boilers in Huai Steel Power Plant being used to remedy coking residual ammonia water (referring to PT-2 type method). The residual ammonia water quality and quantity is shown in Table 1 and the working condition of boilers is shown in Table 2.

Table 1 Coking residual ammonia water quality and quantity

Item	Water quantity, m^3/h	pH	COD, mg/L	Ammonia nitrogen, mg/L	Volatile phenol, mg/L	Cyanide, mg/L
Water quality and quantity	1.5 -2	9.20—9.44	9000—10000	4100—7300	1100—1300	27—34
Existing discharge standard (DB/3200Z006 - 88) in Qingan River, Huaiyin City		6—9	150	30	0.5	0.5

Table 2 Boilers' working condition in Huai Steel Power Plant

Items	Flue gas volume, m^3/h	Outlet temperature, ℃	Fuel composition
Boiler No. 1	34000	175	Blast furnace gas is the main fuel, plus 200—300 kg/h coal
Boiler No. 2	32000	182	Coal is the main fuel (1.4 t/h), plus blast furnace gas

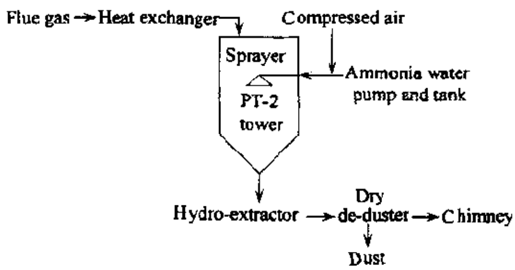


Fig. 1 Technological flow chart of coking residual ammonia water treatment by boiler flue gas

1.1 Technological process

After passing the heat exchanger, the flue gas temperature goes down and goes to tower PT-2, which is a patent equipment with twin flow sprayer. Pressed by pump and mixed with air, the residual ammonia water in tank enters into the sprayer and contacts in the same direction with the flue gas as the state of fog in the tower, and then the physical and chemical reaction takes place (Fig. 1).

All the water in the ammonia water is vaporized under the heat effect of flue gas. Them, the SO_2 in flue gas, NH_3 in ammonia water and O_2 in the tower react to form a $(NH_4)_2SO_4$. Passing hydro-extractor and dust remover, the treated flue gas is emitted from a 40 meters high chimney. The smoke dust can be used for brick or combustion-supporting additive of boiler's fuel. The test results are shown in Table 3.

Table 3 Test results of combustion-supporting additive for the boiler's fuel*

Working condition	Temperature of flue gas, ℃	Pollution concentration in flue gas, mg/m^3			Flame state
		Phenol	SO_2	NO_X	
No additive	123—126	0.03	105—125	0.43—0.46	Normal
Using additive	128—130	0.18—0.20	95—120	0.57—0.60	More roaring
Emission standard (GB 16297 - 1996)		115	700	420	

* Test condition: the test boiler is the boiler No. 1 in Huai Steel Power Plant; the boiler fuel is blast furnace gas; PT-2 tower stopped operation temporarily; input volume of dust additive is 40 kg/h

Since organic substances have the features of higher heat value and automatic combustion-support etc., as a combustion-supporting additive the coal ash absorbed organic substances would improve the full decomposition for the organic substances and would increase the temperature in the high temperature furnace chamber. The test results showed that the smoke dust additive has good combustion supporting and temperature increasing effect, and the burning temperature increases by 4 - 5℃ in average.

1.2 Engineering operation effects

Being treated by flue gas, the zero discharge of coking residual ammonia water is achieved. Whether the polluters such as NH_3, HCN, phenol, benzene, methylbenzene, bimethylbenzene, benzopyrene etc. can be transferred into ambient air or is not one of the key points in this study.

The grounds of standards used in Table 4 and Table 5 are: the SO_2, dust, ringelman blackness based on the "Emission standard for boilers" (GB 13271-91); ammonia follows the "Odor polluters emission standard" (GB 14554-93); all the others are from the "Air polluters' comprehensive emission standard"(GB 16297-1996).

Table 4 Flue gas monitoring results before and after No.1 PT-2 tower

Monitoring polluter	PT-2 tower, mg/Nm^3		Efficiency, %	Standard, mg/Nm^3
	Before reaction	After reaction		
SO_2	216.3	32.6	85	1200
NO_X	2.43	1.17	52	420
Dust	139.1	58.0	58	400
Ammonia	1.31	1.84(<0.06 kg/h)		35 kg/h (40m Chimney)
Hydrogen cyanide	0.043	0.075		2.3
Phenol	0.600	2.646		115
Benzene	nd	0.18		17
Methylbenzene	nd	0.11		60
Bimethylbenzene	nd	nd		90
Benzopyrene	nd	nd		0.5×10^{-3}
Blackness		1.0		1

Table 5 Flue gas monitoring results before and after reaction in PT-2 tower No.2

Monitoring polluter	PT-2 tower, mg/Nm^3		Efficiency, %	Standard, mg/Nm^3
	Before reaction	After reaction		
SO_2	996	177	82	1200
NO_X	4.11	2.11	49	420
Dust	545.2	158.6	71	400
Ammonia	1.74	2.43(<0.08 kg/h)		35kg/h(40m chimney)
Hydrogen cyanide	0.036	0.091		2.3
Phenol	0.780	2.257		115
Benzene	nd	0.21		17
Methylbenzene	nd	0.13		60
Bimethylbenzene	nd	nd		90
Benzopyrene	nd	nd		0.5×10^{-3}
Blackness		1.0		1

All the data in the Tables are the mean value of many monitoring results, which coincides with the result of one-year industrial trial. The monitoring indicates that using flue gas to treat the coking residual ammonia water can not only eliminate all of the coking residual ammonia water and achieve the zero discharge of wastewater pollutants, but guarantee all of the emission factors of flue gas to be up to the emission standard as well.

1.3 Comparison of technical and economical indexes

Comparing above new method with the traditional biochemical method used in Huai Steel Plant, the PT-2 method has obvious advantages in all the technical and economic indexes (Table 6).

Table 6 Comparison of new method with traditional biochemical method

Items	Biochemical method	PT-2 method
Total investment	More than one million RMB Yuan (water volume 1.5 – 2 m^3/h)	700000 RMB Yuan (Water volume 2.2 – 2.7 m^3/h)
Cost for the treatment	300000 RMB Yuan/a	86000 RMB Yuan/a
Area needed	2400 m^2	Much less
Operator	11 persons	One person
Impact extent on water environment	Wastewater discharged is about 150000 m^3/a. COD, ammonia and nitrogen seriously exceed standards, bio-degraded organic pollutants being hardly discharged into Qinggan River	Zero discharge, no secondary pollution
Impact extent on air	Phenol, cyanide, ammonia etc. being trans ferred into air, phenol emission seriously exceeds standard (Table 7)	No ambient air pollution, 180 tons of SO_2 reduced to be discharged per year
Economic benefit		Saving 850000 RMB Yuan each year, including wastewater treatment: 214000 RMB Yuan, discharge fee: 600000 RMB Yuan and SO_2 discharge fee: 36000 RMB Yuan

The gaseous phase composition analysis results (GC-MS) of the Huai Steel Plant coking residual ammonia water showed that the main organic pollutants in the gaseous phase are: benzene, phenol, cresol, bicresol, naphthalene, methylnaphthalene, quinoline, isoquinoline, methylquinoline, indole, methyindole, thianaphthene, benzotetrol, acenaphthene and so on.

It is clear that the aeration process transfers the pollutants in the coking wastewater into ambient air (especially for volatile polluters), which seriously polluted surrounding air around the aeration tanks. For instance, phenol exceeds the standard by 2.3-8.3 times, and the nonattainment ford of hydro-cyanide is 11.7. The PT-2 method, however, has completely eliminated the area source pollution caused by aeration tanks (Table 7).

Table 7 Air pollution monitoring results above aeration tank in the steelplants

Name	Monitoring position	Concentration, mg/m^3		
		Phenol	Hydrogen cyanide	Ammonia
Huai Steel Plant	One meter above the tank	0.93	0.010	2.20
Some large and middle sized steelplants	0.5 – 1.0 meter above the tank	0.33 – 0.65	0.010 – 0.322	1.05 – 3.20
Control concentration limitation of emission standard (GB16297 – 1996)		0.10	0.030	

2 Preliminary examination of mechanism

The key equipment for this new method is the patented PT-2 tower (fog spray drying tower). A series of complicated physical and chemical reactions take place inside the tower between flue gas and foggy residual ammonia water, which include heat transfer, mass transfer, absorption, coagulation, neutralization, catalysis oxidation and catalysis reduction and so on.

2.1 Heat transfer reaction of flue gas

All the water in wastewater is vaporized and zero discharge of pollutants in wastewater is achieved by heat transfer reaction. It is actually the reuse of heat quantity in flue gas. Practice proves that the vaporized wastewater volume is directly related with flue gas volume, flue gas temperature, flue gas temperature difference between inlet and outlet in the tower, wastewater vaporization heat and so on.

Under the industrial trial condition, the vaporization test shows that when the spray volume is less or equal to 1000 l/h, all the water has been vaporized no matter spraying water or residual ammonia water. When the spray volume is more than 1000 l/h, since the residual ammonia water vaporization heat is higher than the water vaporization heat, the ammonia vaporization volume is less than the water vaporization volume. When the spray volume is 1200 1/h, tap water vaporization volume is 1100 1/h, residual ammonia water of that is 1095 1/h.

2.2 Absorption reaction of coal ash

There are coal ash in the flue gas of coal fired boilers, and its main chemical compositions are SiO_2, Al_2O_3, TFe ($FeO+Fe_2O_3$), CaO, MgO and so on. The content range is shown in Table 8.

Table 8 Composition range of coal ash

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Content, %	40 – 60	15 – 40	4 – 20	2 – 10	0.5 – 4	0.1 – 2

In addition, there are also 0.5% – 2% of Na_2O, K_2O and 10% – 30% of unburned carbon in coal ash. The coal ash is formed from high temperature burning in furnace chamber, which is similar to active carbon production. It has rather large specific surface area, which is between 2500 – 5000 cm^2/g or even more (normally more than 2400 cm^2/g). Especially the unburned carbon in the coal ash has a kind of loose and porous structure with lighter bulk density, more specific surface area and a certain of hydropholility. The porous structure and chemical composition make the coal ash also have a certain of solid absorption ability, which can effectively eliminate COD and color of the wastewater. It is widely used in the wastewater treatment. China has started the study and practice in recent years. For instance, using coal ash to treat the wastewater of printing and dyeing (Xiao, 1998), papermaking (Wang, 1995), wool washing (Chen, 1992) and coking (Zhang, 1999) and so on. Coal ash has an absorption degradation effect to the organic substances, which are difficult to be degraded, and ammonia nitrogen polluters in the coking wastewater with a higher degradation rate.

Those substances with mole volume larger than 80 ml such as the organic substances of benzene, methylbenzene, phenol etc. in the coking wastewater, which mole volume is equal to 118, 105 and 95 ml, respectively, are easily absorbed by the active carbon. The quinoline and molysite etc. in the wastewater can improve the absorption effect (Zhang, 1983). By the actual measurement, quinoline makes up more than 20% in some coking wastewater and coal ash contains molysite. They may play the roles of intensifying coal ash, especially for unburned carbon to absorb the cyanide, phenol and benzene in the coking wastewater. The absorption is physical absorption, chemical absorption including catalysis oxidizing absorption.

The fume treated by residual ammonia is almost no pollution impact on ambient air. Its main reason is the coal ash absorption effect to various organic pollution substances in the residual ammonia including physical absorption and catalysis oxidizing absorption.

Table 9 and Table 10 present the results of monitoring, chemical analysis, air phase chromatogram and mass spectrographic analysis for coal ash treated by PT-2 tower, respectively.

Table 9 Monitoring result of fume

Item	Water content, %	COD, mg/kg	Ammonium ion, mg/kg	Volatilie phenol, mg/kg	Cyanide, mg/kg	Sulfate, mg/kg
Concentration	1.94	31300	16840	21	10	19500

The fume produced from Huai Steel Plant coking residual ammonia water treatment project absorbs those pollutants which are mainly mixtures of coal ash and ammonium sulfate produced from chemical reaction in residual ammonia water. Table 10 shows that coil ash has the abserption effect to cyanide, volatile phenol, ammonia ion and other organic substances. With the result that the COD is as high as 31300 mg/kg. Table 10 also shows that the organic substances absorbed in coal ash are primarily polycyclic aromatic hydrocarbons, which are hardly be degraded by biochemical method.

2.3 Coagulation of coal ash

X-ray diffraction analysis shows that besides SiO_2, Al_2O_3 and Fe_2O_3, there are also double salt of silicon and aluminum Al_2SiO_5, $NaAlSiO_4$ in the coal ash. Under the certain conditions, some elements of Al, Fe etc. will become the inorganic salt coagulant. Thus the coal ash is also named as low content inorganic salt coagulant. It can lower the electric potential ζ in the wastewater, and plays the role of wastewater colloid destabilizing (Li, 1994). They quickly deposit into coal ash and improve the absorption effects of coal ash for various organic materials.

Table 10 Analysis result of fume extract by GC − MS

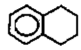
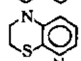
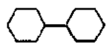
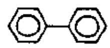
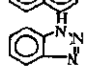
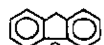
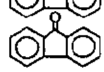
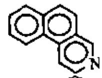
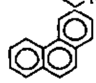
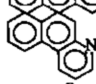
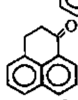
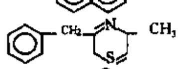
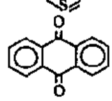
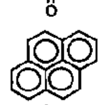
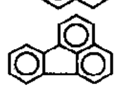
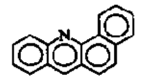
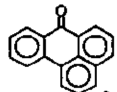
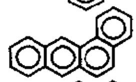
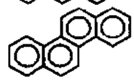
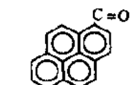
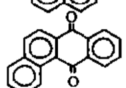
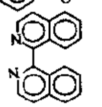
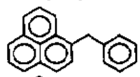
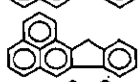
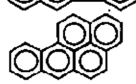
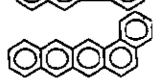
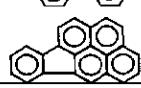
Peak's number	Compound	Structural formula	Molecular weight	Relative content
1	Naphthalinhydrofuran		104	0.12
2	Benzenesulfonamide		135	0.038
3	Quinoline		129	0.12
4	Isoquinoline		129	0.045
5	Dicyclohexane		166	0.21
6	Dibenzene		154	0.065
7	Coumarin		146	0.032
8	Acenaphthylene		152	0.065
9	Benzothiazole		119	0.66
10	Fluorenyl		166	0.072
11	Fluorenone		180	0.19
12	Benzoisoquinoline		178	0.15
13	Phenanthrene		178	0.53
14	Anthracene		178	0.23
15	Benzoquinoline		179	0.25
16	Benzoquinoline		179	0.17
17	Benzoquinoline		179	0.14
18	Perinaphthenone		180	0.19
19	Methylbenzene methythiazole		189	0.54
20	Anthrene		208	0.70
21	Pyrene		202	1.0
22	Benzofluoranthracene		202	0.61
23	Benzofluoranthene		226	0.19

Table 10(cont'd)

24	Benzaridine		229	0.13
25	Benzanthrone		258	0.22
26	Benzanthracene		228	0.44
27	Chrysenyl		228	0.22
28	Formylpyrene		230	0.28
29	Benzanthrone		258	0.22
30	Diquinoline		256	0.16
31	Dinaphthalin		254	0.13
32	Benzofluoranthene		252	0.36
33	Benzopyrene		252	0.093
34	Benzofluoranthracene		252	0.16
35	Benzotetrabenzene		278	0.14
36	Benzoperylene		276	0.085
37	Indenopyrene		276	0.031

Note: Taking the peak value of pyrene as the relative content of 1

2.4 Neutralization reaction of acidity and alkali

In the reaction tower, the acid gases of SO_2, NO_X and CO_2 contained in the flue gas neutralize with the alkali substances of ammonia, pyridine etc. contained in the coking residual ammonia water. The phenol in ammonia water also neutralizes with the CaO in coal ash. Their main reactions are as follows:

$$2NH_3 + SO_2 + H_2O \longrightarrow (NH_4)_2SO_3, \quad (1)$$

$$2NH_3 + 2NO_2 + H_2O \longrightarrow NH_4NO_2 + NH_4NO_3, \quad (2)$$

$$2NH_3 + NO + NO_2 + H_2O \longrightarrow 2NH_4NO_2, \quad (3)$$

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3, \quad (4)$$

$$2C_6H_5OH + CaO \longrightarrow Ca(C_6H_5O)_2 + H_2O. \quad (5)$$

The industrial trial result and Huai Steel Plant production practice demonstrate that treating coking residual ammonia water by flue gas has de-sulfur effect. Consequently, it proves that the Reaction (1) would be one of the main chemical reactions in the tower. Fig. 2 is the relationship between SO_2 concentration in flue gas and test time during the industrial trial period.

2.5 Air oxidization reaction

A volume of 60 – 70 m^3 of compressed air is pumped into TP-2 tower, which makes the oxygen content increase by 8% in the tower. It is the main oxygen source of air oxidization reaction. There are mainly three classifications of air oxidization reactions as follows:

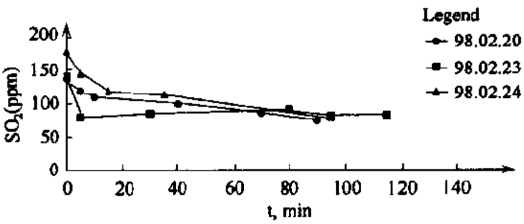


Fig.2 The relationship between SO_2 concentration and test time

(1) $(NH_4)_2SO_3$ oxidized to $(NH_4)_2SO_4$

$$(NH_4)_2SO_3 + 1/2O_2 \longrightarrow (NH_4)_2SO_4. \quad (6)$$

Under the existing condition of Fe, Mg compounds in the coal ash, NO_2 in the flue gas and pyridine in the wastewater, catalysis oxidization may happen in Reaction (6) (Slack, 1977; Ning, 1991).

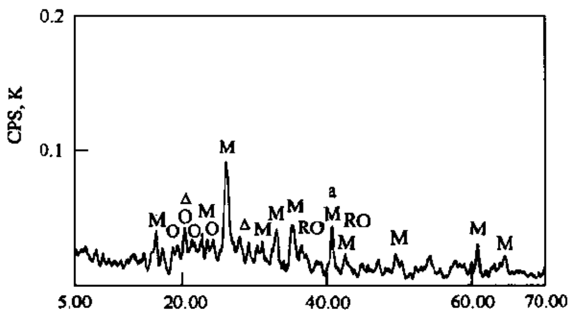


Fig.3 The *X*-ray diffraction figures of coal ash after treating the residual ammonia water
M: $3Al_2O_3 \cdot 2SiO_2$; O: SiO_2; △: $(NH_4)_2SO_4$; α: α-Fe_2O_3; RO: glassiness

The results of *X*-ray diffraction analysis, scanning electron microscope enlargement and chemical analysis have approved the existence of Reaction (6). *X*-ray diffraction analysis (Fig. 3) shows the obvious $(NH_4)_2SO_4$ characteristic peak in the coal ash, and scanning electron microscope enlargement shows the clear crystal edges and corners, and the characteristic peak of $(NH_4)_2SO_4$ has not been found as same as chemical analysis conclusion.

In Fig. 3, the abscissa is the characteristic peak angle, ordinate is the characteristic peak strength.

(2) After oxidization, cyanide is decomposed into NH_4^+ and CO_3^{2-} or NH_3 and CO_2

$$2CN^- + O_2 + 4H_2O \longrightarrow 2(NH_4)^+ + 2CO_3, \quad (7)$$

$$CN^- + SO_2 + O_2 + H_2O \longrightarrow CNO + H_2SO_4, \quad (8)$$

$$CNO^- + 2H_2O \longrightarrow CO_2 + NH_3 + OH. \quad (9)$$

The above catalysis oxidation and decomposition reactions may happen under the coal ash absorption condition. Fig. 4 is the relationship between hydrogen cyanide concentration of flue gas and test time during the industrial trial period.

The industrial trial result and Huai Steel Plant production practice prove that besides coal ash having physical absorption effect to cyanide in the wastewater, there are chemical catalysis oxidation reactions. While its catalysis mechanism needs to be further studies.

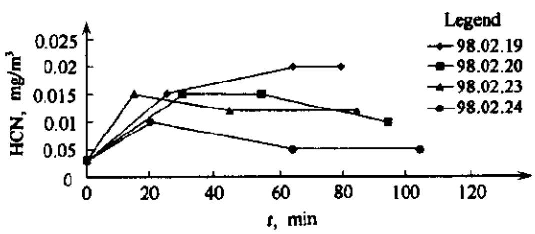


Fig.4 The relationship between HCN concentration in the flue gas and test time

(3) Phenol is oxidized and decomposed into CO_2 and H_2O

$$C_6H_5OH + 7O_2 \longrightarrow 6CO_2 + 3H_2O. \quad (10)$$

Under the existence of molysite and quinoline, Reaction (10) reinforced the absorption of coal ash to phenol. And under the existences of oxygen, Reaction (10) becomes catalysis oxidation and reduction reaction (Zhang, 1983).

The trial result and Huai Steel Plant practice indicated that part of phenol compound in the residual ammonia water is absorbed by coal ash in the form of molecule; part of that is settled in coal ash (Formula 5); and part of that is oxidized into CO_2 and H_2O (Formula 10).

Table 11 is the relationship between volatile phenol concentration in flue gas and test time during the industrial trial period.

2.6 Reaction of oxidation and reduction

The redox reaction occurs mainly between NO_X and SO_2 in the flue gas:

$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O, \quad (11)$$

Table 11 Relationship between volatile phenol concentration and test time

Date (1998)		Concentration of volatile phenol in flue gas, mg/m³					Concentration of phenol in ammonia water, mg/L
	Test time, min.	0	5	50	85	128	
Jan. 13		0.06	1.26	1.74	1.89	1.20	675 (before phenol removing)
	Test time, min.	0	10	45	85		
Feb. 20		0.06	0.60	0.60	0.57		250 (phenol being removed)
	Test time, min.	0	120	170	210		
Feb. 23		0.06	0.30	1.56	2.31		1118 (before phenol removing)
	Test time, min.	0	45	85	120		
Feb. 24		0.06	0.66	0.57	0.96		308 (phenol being removed)

$$8NH_3 + 6NO_2 \longrightarrow 7N_2 + 12H_2O, \quad (12)$$
$$2NO + 2(NH_4)_2SO_3 \longrightarrow N_2 + 2(NH_4)_2SO_4, \quad (13)$$
$$2NO_2 + 4(NH_4)_2SO_3 \longrightarrow N_2 + 4(NH_4)_2SO_4. \quad (14)$$

Formulae (11) and (12) are catalysis oxidation and reduction reactions only on the active carbon surface, or under the existence of catalysts of TiO_2, Fe_2O_3 and Al_2O_3. Since there are 10% – 30% of unburned carbon, TiO_2 and high content of Fe_2O_3 and Al_2O_3 in coal ash, the formulae (11) and (12) have prerequisite to be happened.

Moreover, $(NH_4)_2SO_3$ produced from Formula (1) is a strong reducing agent, and NO_X is oxidizing agent, among which NO_2 is strong oxidizing agent. Redox is happened in the PT-2 tower, and the reactions are as (13) and (14). From Reaction (11) to (14) and together with the Reactions (2) and (3), they are all the de-nitrogen process in the method. Table 4 and Table 5 indicate that the de-nitrogen rate of this method is about 50%.

To sum up the above-mentioned contents, we know that the flue gas heat transfer, coal ash absorption and coagulation effects, acid and alkali neutralization reaction, catalysis oxidation and reduction reactions, air oxidation especially catalysis oxidation reaction are the main mechanisms of de-sulfur and de-nitrogen, pollutants' zero discharge of coking residual ammonia water and meet-standard-emission for the flue gas.

It will be seen from Table 12 where the major pollutants in Huai Steel Plant residual ammonia water are going.

Table 12 shows that PT-2 tower does not exhaust the pollutants such as ammonia, phenol, cyanide etc. into ambient air through dilution. With this method, only 1.0% – 4.7% of pollutants in the residual ammonia water emitted into air, and all others are absorbed by coal ash or eliminated by chemical decomposition.

Table 12 Analysis result on where the major pollutants in the ammonia water going

Major pollutant	Emission into air, %		Coal ash absorption, chemical reaction decomposition, %	
	Boiler No. 1	Boiler No. 2	Boiler No. 1	Boiler No. 2
Ammonia	1.1	1.0	98.9	99.0
Phenol	4.7	2.5	95.3	97.5
Cyanide	2.9	3.1	97.1	96.9

3 Conclusions

Huai Steel Plant production proves that the invention patent "The method of treating all coking wastewater or treating coking residual ammonia water by flue gas" has quite different effects and study train of thought comparing with traditional biochemical method. Pollutants in the wastewater, mainly organic pollutants are separated out from wastewater in solid state, and all the water is vaporized. Consequently, the zero discharge of pollutants in wastewater and waste gas is realized after treatment. Furthermore, there are de-sulfur and de-nitrogen effects on flue gas. This "treating waste by waste" method had the advantages of good treatment effects, lower investment and lower operation cost. It initiates a sustainable development new way for the coking of metallurgical industry.

The mechanism analysis demonstrates that the pollutants' s zero discharge of wastewater by the PT-2 method results from the vaporization effect of flue gas heart transfer; the de-sulfur effect to flue gas is due to acid and alkali neutralization reaction; the de-nitrogen effect on flue gas is the result of acid and alkali neutralization reaction and catalysis oxidation and reduction reaction; while the main reason of flue gas meet-standard-discharge results from the coal ash absorption, coagulation effects and chemical decomposition.

References:

Slack A V, 1977. Waste gas sulfur removal [M]. Translation by Technology Information Department, Shanghai Light Industry Design Institute, China Construction Industry Publish House. 220—230.

Chen D F, 1992. Envronmental Engineering [J], 10(4): 1—5.

Cheng Z J, 1999. The method of treating all coking wastewater or treating coking residual ammonia water by flue gas [P]. Invention Patent No. CN1207367A. Feb. 10, 1999.

Li C C, 1994. Environmental Engineering [J], 12(4): 47—49.

Ning P, 1991. Environment Science [J], 12(5): 10—14.

Wang Y X, 1995. Pollution Control Technique [J], 8(1): 41—44.

Xiao Y T, 1998. Environmental Engineering [J], 16(2): 30—32.

Xu Z R (Translation), 1981. Water quality assessment standard [M], American Envronmental Protection Bureau. China Construction Industry Publish House. No 15.

Zhang C M, 1999. Environmental Engineering [J], 17(1): 16—20.

Zhang F X, 1983. The treatment and utilization of phenol contained wastewater [M]. Beijing Chemical Industry Publish House. 190.

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