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CONVERTER GAS AND WASTE WATER TREATMENT BY OG-SYSTEM IN STEEL SMELTING INDUSTRY

Thesis

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ABSTRACT UNIT Author Date Technology and Business Kokkola-pietarsaari February 2013 Lin Tianyi Degree programme Chemistry and Technology Name of thesis CONVERTER GAS AND WASTE WATER TREATMENT BY OG-SYSTEM IN STEEL SMELTING INDUSTRY Instructor Pages Kaj Jansson 44 Supervisor Kaj Jansson OG system, which stands for Oxygen Converter Gas recovery system, is the suppressed combustion type exhaust gas recovery system for the converters of

Metallurgical industry includes two types of technologies, which are ferrous and non-ferrous metallurgy. There are two smelting methods, combined method (BOF-method) and electric arc furnace method. At present, BOF-method is mainly applied in China, and OG system is mainly applied by most Chinese steel making plants to deal with the waste gas and waste water which are produced by the process of steel making by BOF-method. The purpose of purifying waste water treatment is recycling use. There are three technologies in this treatment, the removal of suspended solid, the stability of the water and the dehydration and reusing of sludge.

steel smelt shops. This system is designed for cooling and purifying the

converter gas which is produced from process of steel smelting.

The purpose of waste water treatment is recycling. The key points of converter gas purifying waste water are: first, the removal of suspended solid; second, the stability of water quality; and third, the dehydration and using of the sludge.

The aims of the thesis were to study the waste water characteristics of iron and steel industry, the properties of the pollutants in the waste water and the process and technology of converter gas and converter gas purifying waste water in steel smelting.

TABLE OF CONTENTS

ABSTRACT

1	INT	RODUCTION	1
2	PO	LLUTION CHARACTERISTICS AND MAJOR POLLUTANTS	3
	2.1	Characteristic of pollutants discharging	5
	2.2	Waste water characteristic and major pollutants	5
	2.3	Major pollutants	5
	2.4	Waste water treatment, reuse and water saving analysis	9
	2.5	Waste water and process discharging analysis	10
	2.6	The analysis of water saving and the reduction of output	12
3	WA	STE WATER TREATMENT AND REUSE TECHNOLOGY	15
	3.1	Waste water sources in steel plant	16
	3.2	Waste water sources in BOF steel making	16
	3.3	BOF waste water treatment technology	18
	3.3	1High-temperature-cooling waste water treatment	18
		2Purifying waste water for converter gas	
4	CO	NVERTER GAS AND WASTE WATER TREATMENT BY OG SYSTEM	
	4.1	Converter gas treatment by OG system	
	4.2	The characteristics of purifying waste water	
	4.3	Variation characteristic of the waste water of converter purification	25
	4.4	Dust content of waste water	
	4.5	The temperature and pH of waste water	
	4.6	Waste water treatment of converter gas purification and reuse technology	
		1The removal of suspended solid	
		2Stability of water quality	
		.3The dehydration and usage of the sludge	
5	CO	NVERTER PURIFYING WASTE WATER TREATMENT PROCESSING	
	5.1	Coagulating precipitation	31
	5.2	Coagulating agent precipitation	
	5.3	Magnetic coagulation precipitation	
6		NCLUSIONS	36
R	EFER	ENCES	39

1 INTRODUCTION

Environmental pollution is one of the biggest problems all over the world at present. From a series of global environmental problems, more and more humans have realized that environment and resources are the basic conditions for the survival and developments of human beings.

Chinese metallurgical industry has been through a dramatic development process; furthermore, Chinese metallurgical industry has reached a brilliant achievement. However, the improvement of Chinese metallurgical industry depends on the Chinese national conditions of metallurgical industries. Compared with global advanced metallurgical industries and countries, there are still much differences in the water saving, pollutant control and waste water treatment. Chinese metallurgical industry consumed too much energy and released too much pollution. Hence, it is quite reasonable to develop and improve green Chinese metallurgical industry to save resources and improve the environment.

Environment protection is one of the most popular international topics. All over the world, people mentioned and gave their own opinions on how to protect the environment and how to improve the air quality and water quality. Furthermore, people can get the information about environment protection from different media platforms. For example, environmental protection advertisements are displayed on television and related articles can be found on magazines and newspapers.

The aim of this thesis is to study the waste water characteristic of iron and steel industry, the properties of the pollutants in the waste water and the technology and process of converter gas and waste water which purify the converter gas in steel smelting. The research questions are: What are the major pollutants in iron and steel waste water? What kind of methods and technologies do steel plants use to deal with the waste water which is produced by the operation of steel smelting? How OG-system deal with the converter gas and waste water which are produced from BOF steel smelting? In my research work, first I start with metallurgy industry, after that I will find out that how steel making plants work, what kind of waster will be produced in the process of steel making, and by what kind of technology and equipment to deal with the waste.

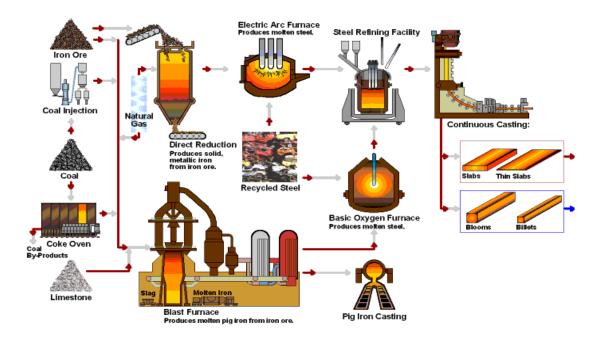
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2 POLLUTION CHARACTERISTICS AND MAJOR POLLUTANTS

Generally, metallurgical industry includes ferrous (iron and steel) and non-ferrous metallurgy (gold, rare metals and light and heavy non-ferrous metals). All kinds of waste water which are produced from metallurgical industry consist of many pollutants which are poisonous and polluted. Furthermore, the waste water must be carefully handled. The purpose of waste water treatment is reducing the amount of waste water, improving the usage of resources, releasing harmless waste water; recycling the waste water and releasing clean waste water. (Wang ZHanwen & Songhua 2008.)

In modern iron and steel industry, there are generally two kinds of technologies, which are "long-process", combined method and "short-process", electric arc furnace method (EAF). For integrated iron and steel plant, the first step is smelt iron and then re-smelt the iron to steel. In this technological process, the raw materials are iron ore, coal, limestone, scrap steel, power resource and other different amount of materials, such as oil, air, chemical compounds, refractory, alloy, water and so on. The iron which comes from the blast furnace is smelted to steel in basic oxygen furnace (BOF), after casting and solidifying; the iron is made to sheet metals, profile shapes, bars and pipes. The output of steel by BOF method is more than 60% in global steel output, integrated steel plant cover a great area, generally produce 300 million tons steel annually, estimated land use 4 to 8 km². Graph 1 shows the main technology of modern large-scale integrated steel plant. Compared with combined method, EAF method apparently covers less area, according to the statistic of international iron and steel institute (IISI), the EAF method plant which produces annually output of iron and steel about 200 million tons covers maximum 2 km². (Wang Zhanwen & Songhua 2008.)

Graph 1 shows the main process of steel smelting in modern large-scale integrated steel plant. In this graph, we can see the steel making processes of both EAF and BOF method. In EAF method, the first step is mixing iron ore and coal which is come from coal injection. After that, transfer the mixture of iron ore and coal into the direct reduction, meanwhile, natural gas is added during the first step. Then, transfer the mixture into EAF, in this step the steel is produced, then transfer the steel into steel refining facility. Finally, the steel products are ready after passing through the continuous casting. BOF method is more complicated, unlike EAF method, the added coal is not from coal injection but coke oven, meanwhile, limestone is added in the first step. The mixture is transferred into blast furnace, then the mixture (liquid) is transferred into BOF, after that, the rest of processes are same as EAF method.



GRAPH 1. Main process of steel smelting in modern large-scale integrated steel plant. (Adapted from The United Nations Environment Programme Industry and Environment Center, 1998)

2.1 Characteristic of pollutants discharging

There are a series of steps in integrated steel plant manufacture. There are different raw materials are inputted in all the produced steps and produced different kinds of waste. liquid waste consist waste water and the harmful substance which contains SS (suspended solid), oil, phenol and so on. Vapor waste are CO₂, SO₂, NO_x, H₂S, CO, VOC and dust. Solid waste is mud, blast furnace slag, converter slag, iron scale and refractory. (Zhaowen, Lei & Yuanlong 2008.)

2.2 Waste water characteristic and major pollutants

Iron and steel industry use a large amount of water resource, and produce waste water during the process of manufacturing, mostly come from producing, equipment and product cooling, equipment and plant cleaning. 70% of waste water come from cooling water, only a small amount of waste water come from the process of manufacture. Basically, the waste water of iron and steel industry are classified as followed: Classification of the major pollutants by property can be classified into organic pollutants. Classification of the pollutants by major content. Classification of the waste water by technology (Zhaowen, Lei & Yuanlong 2008.)

2.3 Major pollutants

Because of the different technologies and methods, the waste water characteristics of iron and steel industry are different. Futhermore, the characteristics of waste water are still different even though smelting methods and technologies are same. For example, the converter gas purifying waste water from top-blown oxygen converter, the steel from same converter but different converting time, the pH of the waste water could between 4~14, suspended solid could between 250~2500mg/L. Indirect cooling water in the

process is polluted only by thermal pollution, usually can be re-used after cooling. Direct cooling water is mixed with materials and products, so it contains same materials, fuels and substances which are according to the complication of the products. The pollutants in the waste water which are produced by iron and steel smelting are classified as followed: (Wang Zhaowen 1998)

Suspended solid (SS) is a major pollutant in the released waste water. Suspended solid is basically formed by iron oxide; the source is from material loading and unloading; the remnant of coke oven treatment device; the waste water treatment device in the process of acid washing and coating and the wet type gas purifying system or waste water treatment system of blast furnace; separately produce coal; biological mud; metallic hydroxides and solid. Suspended solid is also relative to the waste oil which is produced from steel rolling and the released waste water. In normal conditions, these suspended solids are not poisonous in the water (except coke waste water), but they will turn the water to yellow color, reduce the oxygen content in the water and pollute the water. (Wang Zhaowen 1998)

The impact of the metal to the quality of the water has been paid highly attention, therefore, metallic waste water, especially the treatment of heavy metallic waste substance. It can decide if the water can be drinking water, industry and agriculture water, amusement water. The waste water of iron and steel industry contains different levels of heavy metals, for example, the waste water from steel smelting contains high concentrated Zn and Mn. Besides, the waste metals which come from iron and steel production might combine with other poisonous contents such as ammonia, lube, organic compound, alkali and solution. They react to each other and release more poisonous substances which pollute to the environment. (Wang Zhaowen 1998)

In iron and steel industry, waste oil and waste grease mostly are produced from cold-rolling, hot-rolling, casting, coating and scrap steel storage and processing. Because most heavy oil and grease substances are not soluble to water. However, emulsified oil is different; it is mainly applied in cold-rolling operation, which is also an important part of producing process. Normally oil exists in the waste water by four kinds of forms. (Wang Zhaowen 1998)

First, floating oil covers the surface of the waste water, usually in the state of oil membrane or oil layer. The particles of this kind of oil are relative bigger, normally over 100µm, easier to be separated. The lube in the waste water is mainly formed in this condition. Floating oil is major content in the waste water, normally are 80% in the waste water. Second, diffused granular oil, suspended in the water, unstable, normally rest in the water, the size of the granular oil is about 10µm to 100µm. Third, emulsified oil in the waste water is normally in the form of emulsion. The surface of the oil droplets have a stable film which can prevent oil droplets combine together; keep stable for a long time, the size of the oil droplets are relative smaller, between 0.1µm to 10µm, mainly are between 0.1µm to 2µm. Emulsified oil is major pollutant in steel rolling waste water. Fourth, dissolved oil is used to dissolve particles by chemical method; the size of oil droplets is even smaller than emulsified oil. Normally, oil and grease are not poisonous, but it can change the surface color of the water, reduce the conductivity of the water, seriously damage the fish in the water and aquatic life, when oil concentration in the lake, river is 0.01mg/L, there is special smell exist in fish meat, if oil concentration is higher will result to the death to the fish. The scales (FeO, Fe₂O₄, Fe₂O₃) which on the surface of the steel product are all alkaline substances (oxide) that are insoluble to the water, when putting them in acid solution, these oxides and acid will generate a series of reactions. (Wang Zhaowen 1998)

Sulfuric acid and hydrochloric acid are normally applied to steel pickling. For stainless steel pickling, the mixed acid solution which contains nitric and hydrofluoric acid is mainly used. In the process of pickling, due to the oxidation reaction of acid that in the pickling solution and iron, the concentration of the acid keep reducing, oppositely, the content of iron salt keep increasing. When the concentration of the acid reduces to a certain point, the pickling solution must be replaced; hence, the pickling waste is formed. The steel products which have been pickled should be washed by the water in order to remove the free acid and iron salt which on the surface of the steel products. The water which washed the steel products, produce waste water which contains low concentration of acid. (Wang Zhaowen 1998)

Acid waste water is strongly corrosive, is freely corrode pipes and constructions; release to the water, change the pH of the water, reduce the self-clean ability of the water, and affect aquatic life and fishery; release to farmland soil, freely acidize the soil and damage the crops. The waste water should be handled by neutralization, and control the pH of the waste water in the scope of 6 to 9, after that, the waste water can be released into the water. (Zhaowen, Lei & Yuanlong 2008.)

Iron and steel industry release more organic pollutants than some other industries. For example, the process of coking will produce different kinds of organic substances, which include benzene, methylbenzene, dimethylbenzene, phenol,PHA, The analysis proposes that there are 52 kinds of organic substances in coking waste water. (Zhaowen, Lei & Yuanlong 2008.)

The organic substances which are produced by steel smelting plant include benzene, methylbenzene, dimethylbenzene, polycyclic aromatic hydrocarbons (PAH), PCB, phenol. If wet-type gas purifying method is applied for these substances, they will inevitably exist in the waste water. (Zhaowen, Lei & Yuanlong 2008.)

2.4 Waste water treatment, reuse and water saving analysis

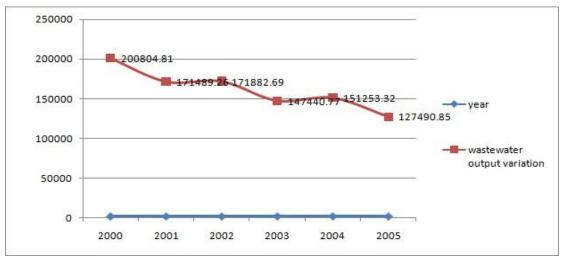
Since1970s, environmental protection of Chinese iron and steel industry has been through more than 30 years of development and reached a huge achievement. Less pollutants output which is the premise and foundation to keep developing of Chinese iron and steel industry. Especially the import of steel products and the creation of environmental protection technology by Baosteel (Chinese steelmaking plant), which gave an excellent environmental protection example to Chinese iron and steel industry. Baosteel steel plant is a milestone in the history of Chinese iron and steel industry. The environmental protection technology of Baosteel has reached the world's advanced level. However, for the whole Chinese iron and steel industries, there are still differences in the environmental protection compared with developed countries` advanced technologies. Hence, iron and steel industry is still a major polluter in the whole Chinese industries. According to relevant investigation reveals, in 2005, iron and steel industry waste water output is 10% of output of Chinese major industrial waste water, hence, the waste water treatment and reuse is still a hot topic in Chinese iron and steel industry. (Wang Zhaowen & Yang Jingling 2008)

year	steel output	water consumption	new water input	rate of reusing
	million/t	m³/t	m ³ /t	%
1996	8789	231.92	41.73	82.01
1997	951.929	220.46	37.63	82.93
1998	10444.45	213.25	34.17	83.97
1999	11128.07	192.82	28.79	85.07
2000	11697.89	191.12	24.75	87.04
2001	14656.3	161.01	17.78	88.85
2002	16860	147.79	14.89	920.32
2003	22000	114.52	13.73	90.63
2004	27300	111.06	11.27	92.15
2005	34936	111.56	8.6	94.04

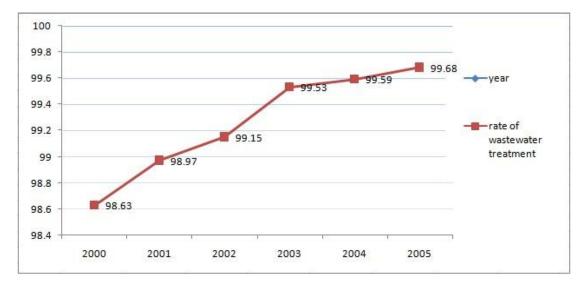
TABLE 1. The amount of water use and rate of reuse in iron and steel industry from 1996 to 2005 (adapted from Wang Zhaowen & Yang Jingling 2008)

As we can see from table 1, from 1996 to 2005, the amount of water consumption in iron and steel industry reduced from 231,92m3 to 111,56m³. Steel output reduced to 3120,36m³, rate of reduction is 52,1%. Water consumption is reduced from 41,73m³ to 8,6m³. New water input is reduced 33,13m³, rate of reduction is 79,4%. Rate of reusing is increased 12,03%. (Wang Zhaowen & Yang Jingling 2008)

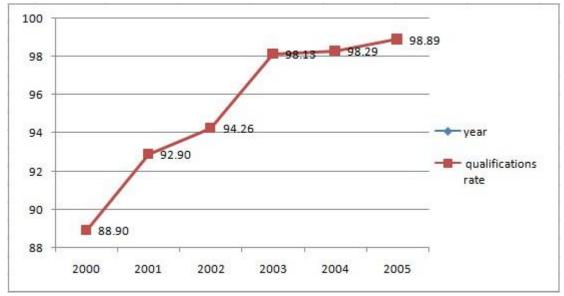
2.5 Waste water and process discharging analysis



GRAPH 2. Waste water output variation from 2000 to 2005 (adapted from Wang Zhaowen & Yang Jingling 2008)



GRAPH 3. The rate of waste water treatment in Chinese iron and steel industry from 2000 to 2005 (adapted from Wang Zhaowen & Yang Jingling 2008)



GRAPH 4. The qualifications rate of waste water output (adapted from Wang Zhaowen & Yang Jingling 2008)

As we can see in graph 2, from 2000 to 2005, the amount of waste water output of Chinese iron and steel industry is reduced year by year, from 2008.0481 million tons reduced to 1274.49085 million tons, rate of reduction is 36.5%. In graph 3, the rate of waste water treatment is increased annually, which is increased from 98.63% to 99.68%. In graph 4, the rate of qualifications rate is increased from 88.90% to 98.89%. Furthermore, from year 2000 to 2005, according to the investigation, in the released waste water

by iron and steel industry, the situation of major pollutants are shown by the table 2 as below: (Wang Zhaowen & Yang Jingling 2008)

TABLE 2. The major pollutants in the released waste water of iron and steel industry, 2000 to 2005 (adapted from Zhang Jinglai & Wang Jianbo 2008)

year	COD/t	suspended solid/t	petroleum/t	phenol/t
2000	115147.59	356730.97	7663.43	318.62
2001	85520.04	155506.54	6244.8	181.61
2002	87261.25	146667.06	5905.75	153.84
2003	83735.41	170397.11	5446.33	192.71
2004	79825.85	137072.55	4677.71	128.25
2005	65386.63	143509.73	4107.05	123.08

As we can see from table 2, in our national iron and steel waste water, every major pollutant is obviously reduced; especially suspended solid is the most reduced. From 2000 to 2005, the suspended solid is reduced from 356730.97 tons to 143509.73 tons. Phenol is reduced from 318.62 tons to 123.08 tons. (Wang Zhaowen & Yang Jingling 2008)

2.6 The analysis of water saving and the reduction of output

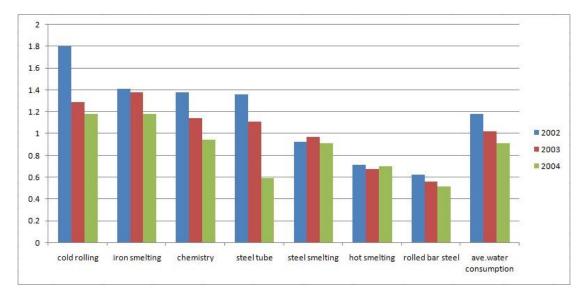
Since 2000, in Chinese iron and steel industry, the realization of the importance of water saving has been highly improved. Chinese government invested more facilities and money on water saving, iron and steel industries are much improved in water saving. Compared between the year 2000 and 2005, the output of steel increased from 117 million tons to 349 million tons, the rate of increase is 198.65%, but rate of water use only increased 74.3%. New water input to per ton of steel reduced from 24.75m³/t to 8.6m³/t, reduction rate is more than 65%. Waste water reusing rate increased 7%. (Wang Zhaowen & Yang Jingling 2008)

In order to control and analyse the way to save more water, one of the most famous iron and steel company set one systematic water-balance test and analysis in every step of iron and steel manufacture, which contains water input, water output, cooling water, cycling rate, new water input and waste output. The water use and water consumption in every step of iron and steel manufacture are shown by the table 3 and graph 5 as below: (Wang Zhaowen & Yang Jingling 2008)

User	vear 2002	year 2003	year 2004 Jan to May
Chemical companies	562.9		
Iron-smelting	1187.4		
Steel-smelting	802.4	869.8	825.1
Rolled bar Steel	100.1	76.4	63.3
Steel tube	85.9	69.3	36.9
Hot rolling	502.2	458.1	446.7
Cold rolling	615.3	626.1	610.6
Energy department	504.5	589.8	549.8
Other department	240.7	255.8	257.9
Construction water	97.3	83.1	50.1
Water lose	430.3	429.3	324.9
Total: kilotons/month	5123.9	5175.5	4726.5

Table 3. The amount of water used in every section (adapted from Wang Zhaowen & Yang Jingling 2008)

From table 3 we can see iron-smelting use much more water than any other sections on the table. In 2002, the water consumption of iron-smelting is 13.8 times more than the amount of water used by steel tube, which is only 85.9 kilotons. In 2003, the ratio of water consumption between iron-smelting and steel tube is increased to 16.4. (Wang Zhaowen & Yang Jingling 2008)

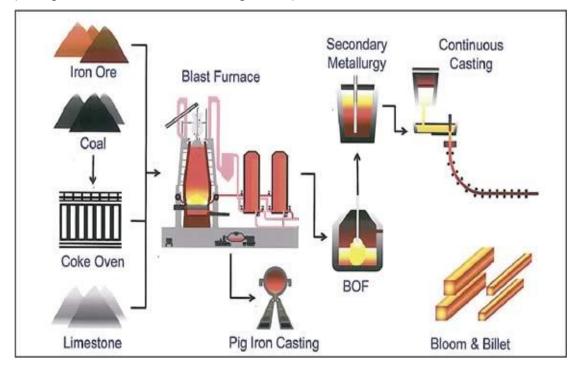


GRAPH 5. The water consumption in every section, unit: m³/unit production (adapted from Wang Zhaowen & Yang Jingling 2008)

According to the statistic analysis from graph 5, in 2002, the section of cold rolling use more water than any the other section. The water consumption of cold rolling is 3 times than rolled bar steel. In 2004, the ratio of water consumption between cold rolling and rolled bar steel is 2.2. Furthermore, the water consumptions in all the sections are reduced year by year. (Wang Zhaowen & Yang Jingling 2008)

3 WASTE WATER TREATMENT AND REUSE TECHNOLOGY

Steel smelting (steel making), is the process of reducing the higher contents such as C, Si, P and Mn in iron. With the development of steel smelting technologies and the request of steel types, and improvement of secondary refining and smelting equipments, the whole steel smelting processes are generally simplified to steel making, secondary refining and continue casting. (Wang Zhaowen & Zou Yuanlong 2008.)



GRAPH 6. Process of steel making by BOF method. (Glad stone steel project 2009)

Graph 6 shows the process of steel making by BOF method. The main producing departments are: oxygen converter department, secondary refining department and continues casting department. Main facilities in a steel plant are: water station, oxygen station, air-pressure station, boiler room, water treatment facilities and electricity generator and power distribution system. The raw materials are iron ore, coal and limestone, they will be mixed together and transferred into blast furnace. After the mixtures are melted, it will be transferred into basic oxygen furnace, after that the steel are made. After the rest of process, the steel products are made. (Wang Zhanwen & Zou Yuanlong 2008)

The water input and waste water in a steel plant are more complicated, generally classified into: Indirect cooling circulating water system. Direct cooling circulating water system. Industry waster system. Salt collection water system. Series-connecting water system. Producing waste water & sludge treatment system. Other. (Wang Zhanwen & Zou Yuanlong 2008)

3.1 Waste water sources in steel plant

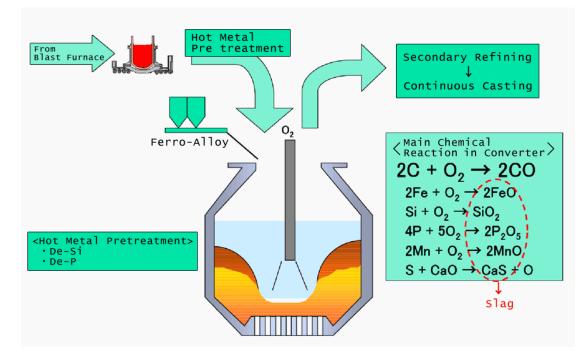
Generally, different steel making operations, system structures and water resources result to different waste water. The waste water sources are classified as followed: Oxygen top-blown converter (BOF) waste water. Converter gas indirect cooling waste water. Converter gas purifying waste water. Continues casting machine waste water. Equipment indirect cooling waste water. Equipment and products direct cooling waste water. Dust cleaning waste water. Converter steel slag cooling waste water. Other (Wang Zhanwen & Zou Yuanlong 2008)

3.2 Waste water sources in BOF steel making

Basic Oxygen Furnace (BOF), also known as Basic Oxygen Steelmaking (BOS), Basic Oxygen Converter (BOC), is a steel making furnace which molten steel scrap and pig iron converted into steel by oxygen blown into the melt under a basic slag. The overall output of steel by BOF method is more than 60% in global steel output. (Zhaowen, Yuanlong & Xiaoli 2008)



GRAPH 7. General looking of BOF (Boulder Steel 2009)



GRAPH 8. Main reaction in the converter (Zhaowen, Yuanlong & Xiaoli 2008) BOF (basic oxygen furnace) will generate a large amount of high temperature

gas which contains carbon oxide and iron oxide dust. In this high temperature gas, the concentration of CO is over 90% and there is 70% of FeO in the dust. Hence, cooling and purifying the high temperature converter gas is an very important technology and operation for collecting gas (CO), waste heat and iron oxide dust. This operation contains two steps which are cooling the high temperature converter gas, and purifying the converter gas which has been cooled by first step. (Zhaowen, Yuanlong & Xiaoli 2008)

The waste water is produced from these two steps. The waste water from first step is called high temperature cooling waste water, because it has no direct contact with the gas, so it is also called indirect cooling water for equipments. The waste water from second step has direct contact with the gas, so it is called waste water of converter gas purifying. (Zhaowen, Yuanlong & Xiaoli 2008)

3.3 BOF waste water treatment technology

Steel making by BOF method will produce high-temperature-cooling waste water and waste water for purifying the converter gas. Each waste water has different treatment. Each treatment has different equipments and technologies. Because high-temperature-cooling waste water has no direct contact with the gas, so it is much easier to deal with than the waste water for purifying the converter gas. (Zhaowen, Yuanlong & Xiaoli 2008)

3.3.1 High-temperature-cooling waste water treatment

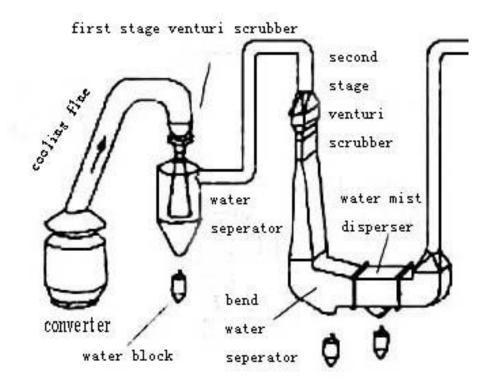
Converter high temperature system contains moveable skirt, fixed hood and smoke flue. Water circulating cooling must be applied in this system. Furthermore, the vapor which is generated from high-temperature-cooling process will be collected and dominated. Cooling the converter gas by OG system, closed-hot-water-circulating cooling system is applied on moveable skirt and fixed hood, forced-vaporizing cooling system is applied on the flue. The above water and gas do not have direct contact with the converter gas, and could be reused after cooling. (Zhaowen, Yuanlong & Xiaoli 2008)

3.3.2 Purifying waste water for converter gas

After the converter gas passed through the moveable skirt, fixed hood and flue, the temperature of converter gas will be reduced from 1450 degrees to less than 1000 degrees. The next step is purifying system of converter gas. OG purifying system generally contains two stage venturi scrubber, separator which is a 90 degrees bended water pipe and water mist disperser. Purifying waste water is the main waste water of steel making operation, the waste water contains a large amount of waste water, high concentrated suspended solid and complicated composition. Sludge will be the raw material for iron smelting after evaporating and dewatering. The gas will be sent to the user after purifying. (Zhaowen, Yuanlong & Xiaoli 2008)

Although LT-system has several advantages, and technologies is not only successful but also mature. However, most steel making plants choose OG-system to cool down the temperature of the converter gas and purify the gas. In chemistry, carbon oxide gas is an inflammable and explosive gas. There are two conditions which can result to the explosion and combustion of gas. First, mixing the gas with the air (actually the oxygen in the air). Second, spark can light the gas. LT-system purifies the converter gas by using high-voltage-static dust catcher. In the process of purifying the converter gas by LT-system, the static sparks are generated unavoidably; there is a large amount of oxygen is blown into BOF steel making converter, on the other hand, air also easier float into the system through the hood. In this case, purifying carbon oxide by using high-voltage-static dust catcher is more dangerous to

operate. This is the main reason why most steel-making plants do not choose LT-system. And that is also the main reason why OG-system is more welcomed by most steel-making plants. (Zhaowen, Yuanlong & Xiaoli 2008)

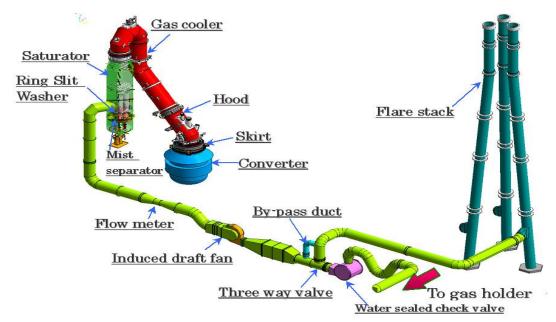


GRAPH 9. General structure of converter gas treatment (adapted from Zhaowen, Yuanlong & Xiaoli 2008)

Graph 9 shows the general structure of converter gas treatment. When the converter is working, it generates the converter gas; first of all, the converter gas will float into cooling system for cooling down the temperature of the gas. Second, the gas is purified by purifying system and separated the liquid and gas by water separator. After that, the gas float through the second stage venture scrubber and water mist disperser. (Zhaowen, Yuanlong & Xiaoli 2008)

4 CONVERTER GAS AND WASTE WATER TREATMENT BY OG SYSTEM

OG system, which stands for Oxygen Converter Gas recovery System, is the suppressed combustion type exhaust gas recovery system for the converters of steel makings shops. Since 1962, the OG system has been jointly developed and improved by both Nippon Steel corporation (NSC) and Kawasaki Heavy Industries Ltd. (KHI). In 2004, the technologies were succeeded to JP Steel Plantech Co. (SPCO), and ever since, SPCO continued to supply the technologies of OG system all over the world. Until now, more than 180 OG systems have been installed all over the world. (Jp Steel Plantech Co. 2009)



GRAPH 10. The structure of OG system (JP Steel Plantech Co. 2009)

The OG system, being installed just above the converter mouth, has functions to cool down, to clean up and to recover exhaust gas (mainly CO gas) with suppressed combustion rate. The OG system can ideal solution to the customers in terms of both energy saving and environmental control recognized generally as recent trends. (Jp Steel Plantech Co. 2009)

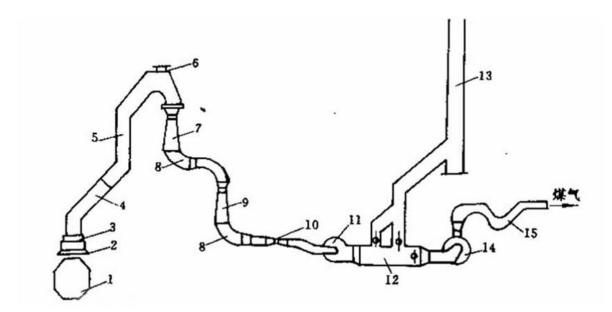
OG system has following features: first, compact, suppress combustion rate of LD gas, OG system structure is much more compact than full-combustion type system that makes it possible to realize flexible arrangement with correspond to site. Second, high performance of hood gas pressure control by RSW. RSW (ring slit washer) has a high efficiency of dust collection. Also, it has a role in controlling pressure in the hood. Its high response and high reliability can prevent puffing out the exhaust gas from the converter's mouth and air intrusion, which achieves low combustion rate constantly. Third, hight dust collecting performance. RSW, venturi scrubber type as a dust collector of OG system can keep high dust collecting performance even under frequent change of gas flows during blowing time. Fourth, high safety, OG system can treat safely explosive exhaust gas (CO) because all the surface of ducts in OG is always moist condition so that there is no source of burning anytime. Fifth, energy is recovered effectively. OG system can recover latent heat of highly concentrated CO gas (exhaust gas) and sensible heat by OG boiler. Moreover, by applying convection boiler, more sensible heat (steam) can be recovered. (Jp Steel Plantech Co. 2009)

The waste water for purifying the converter gas is used to clean the high temperature gas which is generated by the process of BOF steel making. There are several kinds of waste water are produced by different steps of steel smelting. In this section, I only concentrated on the converter gas and the treatment of the waste water for purifying the converter gas by OG system. (Jp Steel Plantech Co. 2009)

4.1 Converter gas treatment by OG system

In the process of BOF steel smelting, because oxygen is blown and mixed with the iron liquid, there is a large amount of high temperature gases came out through the month of converter, and float into the flue through the hood. This process will reduce the temperature of gas. After that the gases will float to the purifying system which contains two-stage venturi scrubber. The gases in turn pass through first and second stage venturi scrubbers. In this process, the dust of gas will be removed, and meanwhile, the temperature of the gas will be reduced again. This is the general process of converter gas treatment. (Pei Haibin 2005)

The OG purifying system for cleaning the gases which are produced from BOF steel smelting, two-stage venturi scrubber is applied. The contents of the converter gases depend on the selection of treatment methods and systems. In steel and iron industry, steel smelting is an oxidation reaction to reduce the contents of iron and other elements. The carbon in the iron liquid reacts with oxygen and generates carbon oxide, and then it floats out of the converter with converter gas. Close the mouth of the converter, carbon oxide will still exist in the same form after the converter gas passes through the vaporizing-cooling flue. The converter gas will be recycled as a part of energy resources of the factory. This kind of converter gas is called converter coal gas. This gas treatment process is called recycled method, or unburned method. (Pei Haibin 2005)



1-converter 2-skirt 3-lower hood 4-upper hood 5-vaporizing co 6-explosion doo 7-first stage venturi 8-elbow water separator 9-second stage venturi 10-gas meter 11-exhaust fan 12-three-port valve 13-flare stacl 14-Water converter 15-V-type water-sealed valve

GRAPH 11. Purifying process of the converter gas by unburned method (adapted from Zhaowen, Yuanlong & Xiaoli 2008).

The purifying process of the converter gas by unburned method is shown in graph 11. If the converter mouth is open, it results to a large amount of air leaks into the flue with the converter gas through the gate of the flue. In the flue, the oxygen from air reacts with the carbon oxide from the converter gas to combustion reaction. Most carbon oxide transformed to carbon dioxide, and generates heat at same time. Furthermore, it also increases the temperature of the inner flue. This kind of converter gas, after a part of heat is collected and passed through venturi scrubbers, purified and cooled; the converter gas has to be released because it is no longer valuable to be collected. This method is called burned method, which is rarely used. Both converter gas treatment methods result different consequences. (Pei Haibin 2005)

4.2 The characteristics of purifying waste water

BOF steel smelting is an intermittent operation. The process is iron liquid loadoxygen blow- slag materials add- oxygen blow- steel finish. After these steps, one furnace of steel has been smelted; modern BOF steel smelting will take approximately 40 minutes, which contains 18 minutes for oxygen blowing. Because the features of different steps, the amount of gas in the converter, temperature and complications keep changing during the process of steel smelting, hence, the changing of the characteristics of the purifying waste water is the most important characteristic. (Pei Haibin 2005)

4.3 Variation characteristic of the waste water of converter purification

Purification is a very conflictive process. A large amount of dust in the gas floated into the water through the cleaning of two stage venturi scrubbers. In the words, the gas is changed from vapor phase into liquid phase after passed through the purifying equipment. As above, the concentration of dust in the gas is always changing; hence, the concentration of suspended solid in the waste water of converter purification is always changing. Normally, the concentration of suspended solid in the waste water of converter purification is always changing. Normally, the concentration of suspended solid in the waste water of converter purification is approximately between 5000- 15000mg/L. (Pei Haibin 2005)

Different operations of converter gas treatment result to the different characteristics of the waste water of converter purification. In non-combusting operation, the major suspended solid in the waste water of converter gas purification is FeO. The color of the waste water is gray, the particle size of suspended solid is big. The pH of the waste water is more than 7, sometime can be over 10. In combusting operation, due to the reaction of combustion by CO and O_2 in the flue, results to FeO react to Fe₂O₃, the particles of suspended solid are smaller than first operation (because breaking exists in

the combusting reaction). The color the waste water is red. In normal conditions, the pH is under 7, acidic, some waste water is alkaline, which is because a large amount of lime powder is mixed. (Pei Haibin 2005)

4.4 Dust content of waste water

During the process of steel smelting by BOF, due to the boiling and volatility of Fe, the mixing of oxygen and ejection of carbon oxide, there are a large amount of converter dust are produced. Dust content is approximately 1%~2% of metal input. Converter gas content changes over time; normally, the dust content and variation of converter gas reach their maximum points when oxygen is blowing into the converter. (Pei Haibin 2005)

4.5 The temperature and pH of waste water

The temperature of waste water changes over the temperature of converter gas in the smelting operation. Usually, the temperature of waste water is higher when oxygen is blowing. The impact of the pH of purifying waste water of the converter gas is related to the purifying method of converter gas. The waste water which is produced by combusting method, because the acidic gases such as CO_2 , SO_2 in the gas are dissolved into the water, lower the pH of the waste water. The waste water which is produced by non-combustion method, due to there are not too much acidic gases in converter gas, it has low impact for the pH of the waste water. Besides, adding more lime powder to the process of steel smelting can raise the pH of the waste water, and make it alkaline. (Pei Haibin 2005)

4.6 Waste water treatment of converter gas purification and reuse technology

Reuse is the purpose of the waste water treatment of the converter gas purification. The key points of the waste water of converter gas purification are. First, the removal of suspended solid. Second, the stability of water quality, third, the dehydration and usage of the sludge. (Pei Haibin 2005)

4.6.1 The removal of suspended solid

Both natural precipitation and forced precipitation can be used in removal of suspended solid from the purifying waste water of converter gas. Natural precipitation can reduce the concentration of suspended solids between 150~200mg/L, but the performance of reuse is not quite ideal. In this case, forced precipitation is normally used in this process. The most popular way of the removal of suspended solid from waste water is adding water treatment coagulant to the precipitation tank, or first magnetizes the waste water and then flow into magnetic coalescer. This is another more ideal and effectively method. (Pei Haibin 2005)



GRAPH 12. The basic structure of hydrocyclone (adapted from Jiangxi Gand, 2013.)

The waste water first flow into the hydrocyclone, remove the bigger sizes of suspended particles (over 60µm) by using gravity separation principle, in order to reduce the load of the precipitation tank. Adding polyacrylamide can reduce suspended solids in the waste water under 100mg/L, and then, the waste water can be normally reused. Iron oxide is magnetic substance, so it can be handled by magnetic-forced separation method. (Pei Haibin 2005)

4.6.2 Stability of water quality

Lime is added into the process of steel smelting, when oxygen is blowing. Some lime powders are blown out of the convert before mixing with steel liquid. The lime powders flow into the purifying system with the converter gas, hence, the content of Ca^{2+} in the waste water is high. Lime powders react with CO_2 in the water temporally increased the hardness of the waste water, so the waste water is unstable. Adding sodium carbonate (Na₂CO₃) is an effective way to stabilize the water quality. Na_2CO_3 reacts with lime [Ca(OH)₂] generates precipitation of CaCO₃. (Pei Haibin 2005)

$CaO + H_2O \rightarrow Ca(OH)_2$

$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH$

The produced NaOH react with CO_2 in the water and produce Na_2CO_3 , Na_2CO_3 is re-produced in the reaction. (Pei Haibin 2005)

Mixing the cleaning water and purifying waste water of the converter gas is also another effective way to keep water quality stably. Converter gas contains a large amount of HCO_3^- and the waste water of converter gas purification contains a large amount of OH^- , the reaction is given as followed:

$Ca(OH) + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$

The produced calcium carbonate will be removed in the precipitation tank. This is a classical waste- waste type treatment. In short, the method and technology for stabilizing the water quality should be selected according to the condition of manufactories and water quality. Furthermore, the most effective and economic way should be selected according to different situations. (Pei Haibin 2005)

4.6.3 The dehydration and usage of the sludge

The precipitated sludge must be handled and reused. Otherwise the purpose of the reuse of waste water of converter gas will never come true. The sludge in the waste water contains 70% of iron, which has a very high application value. The way to handle this kind of sludge is the same as the way to handle the gas sludge which is produced from the waste water of converter gas. In China; vacuum filtration is mainly applied, but this method has a serious disadvantage, because the sludge particles are small, and high alkaline, which results to a nonideal performance of filtration. At present, more and more companies stop using this method. Oppositely, pressure filter filtration is became more welcomed by companies, because it performs better in filtration. Compared with vacuum filtration, pressure filter filtration is more expensive to apply than vacuum filtration. But pressure filter filtration performs more ideal than vacuum filtration on filtrating ability. Even though the price of operation is higher, but in China, high performance is more welcomed by most iron and steel industrial factories. (Pei Haibin 2005)

5 CONVERTER PURIFYING WASTE WATER TREATMENT PROCESSING

At present, there are different kinds of treatment processes and methods of waste water of converter gas in different companies or factories. Most factories and companies will choose the best treatment process and method according to the conditions and features of the companies and factories. There are three kinds of more successful and effective treatment processes and technologies for the waste water of converter gas purification. (Zhaowen, Yuanlong & Xiaoli 2008)

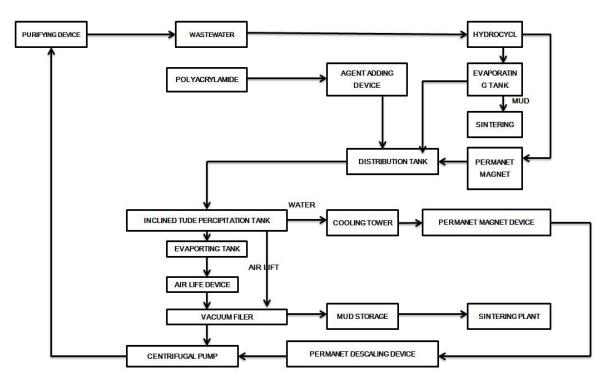
5.1 Coagulating precipitation

Stabilizing agent of water treatment and reusing process is used in coagulating precipitation. The purifying waste water which is released from first stage venture scrubber flow into the separation tank through an opening channel, separated out the bigger size of particles which are 15% of content and over 60µm in the particles separation tank by separating machine, the separated particles are sent to sintering plant for reusing; the waste water which contains smaller particles flow into the precipitation tank. After that, added flocculating agent to the waste water in the precipitation tank to finish coagulating precipitation operation. (Zhaowen, Yuanlong & Xiaoli 2008)

After the operation finish, the waste water will flow out from precipitation tank and delivery by circulating water pump to second stage venture scrubber for use. Pressing the outflow of second stage venturi scrubber, and then send the outflow to first stage venturi scrubber for series-use, add anti-scale agent (water stabilizer) to the outflow pipe of circulating water pump, in order to prevent the equipments and pipes are rusted. After dehydrated the sludge where under the precipitation tank, the dehydrated sludge is sent to sintering plant, and sinter the dehydrated sludge into spheres and circulating use. In coagulating precipitation, the key point of this treatment process is that separate out the bigger particles (15% of content and over 60µm) in separation tank to prevent pipe is plugged. (Zhaowen, Yuanlong & Xiaoli 2008)

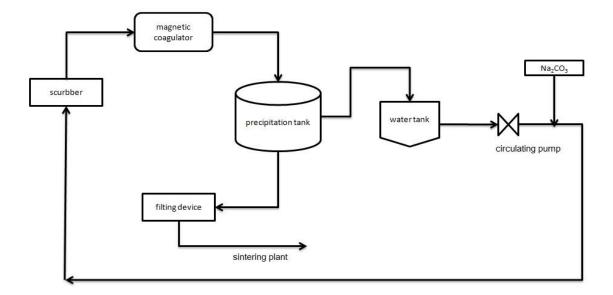
5.2 Coagulating agent precipitation

The waste water of converter gas purification flow into hydrocyclone via opening channel, iron mud are used by sintering plant after the iron mud has been evaporated. graph 13 shows the process of waste water treatment of permanent magnet descaling (Zhaowen, Yuanlong & Xiaoli 2008 P146)



GRAPH 13. The process of waste water treatment of permanent magnet descaling (adapted from Zhaowen, Yuanlong & Xiaoli 2008 P146).

The outflow from upper of the permanent magnet will be handled by permanent magnet. After that, the outflow flows into distribution pool and mixes with polyacrylamide solution, then flows into inclined tube precipitation tank. The temperature of outflow will be cooled by cooling tower and flows into water collecting tank. Pure water flows through magnetic scaling equipment, and then to be pressured and recycled. The mud from the precipitation tank will be sent to evaporation tank by mud pump, and evaporated mud goes to vacuum filter dryer, the mud has approximately 40%~50% water content, and finally the mud is sent to sintering plant. (Zhaowen, Yuanlong & Xiaoli 2008 P146).



5.3 Magnetic coagulation precipitation

GRAPH 14. Process of water stable agent treatment (adapted from Zhaowen, Yuanlong & Xiaoli 2008 P146).

The waste water of converter gas purification flow into precipitation tank after coagulated by magnetic coagulator, and adds sodium carbonate into the outflow of precipitation tank, in order to solve the problem of water quality for reuse. The mud under the precipitation is sent to van-type filter press in order to dehydrate the water from the mud. Water content in the dehydrated mud is low enough to be reused by sintering plant. The process is shown in graph 14. (Zhaowen, Yuanlong & Xiaoli 2008 P146).

In China, most iron and steel companies smelt steel products by using BOF system. There are mainly four kinds of converter gas purifying waste water treatment. Converter gas is purified by using two stages venturi scrubbers. The outflow of first stage venture scrubber pass through particles separator and flow into precipitation tank. After precipitated by mixing with coagulating solution the outflow is pressured by pump and sent to second- first stage venturi scrubber for circulating reuse, and mud is dehydrated by pressure filter, and after that, collected and reuse. (Xiao Xingxuan 1993)

Converter gas is purified by using two stages dust separator. For the waste water treatment, not too much different with the first process, only the outflow of the precipitation is cooled down by cooling tower and sent to second stages dust separator for recycling. After the mud is evaporated, it will be dehydrated by vacuum filter. There are more structures in this type of waste water treatment system, but the rate of dehydrating is quite low, and the water content in the waste water is over 40%. (Xiao Xingxuan 1993)

After the waste water passed through hydrocyclone and vertical precipitation, it will be pressured and cooled by the cooling tower, and finally used as purifying water. In this system, by adding coagulant, the water is reused. The mud which comes from precipitation will be first evaporated and then dehydrated by vacuum filter. In this type of waste water treatment system, the rate of precipitation in the waste water is quite low, but the rate of water content in the mud is quite high, it brings a quite serious problem for the dehydration of the mud. The performance is not ideal. (Xiao Xingxuan 1993)

Converter gas float through flooded venturi, dehydrator, multi-throat venturi and turbulent tower, and purifying waste water is precipitated and cooled for reuse. Mud is dehydrated by internal filtration type vacuum filter. Those four kinds of converter gas and waste water treatment system above, the performance is relative to the selection of system, and the levels of management. But there are still different kinds of problems. All the related engineers keep improving the treatment systems. Mainly, they keep trying to improve the precipitation of suspended solid, dehydration of mud and water quality stabilization technologies, in order to achieve the aim of efficient waste water treatment and improve the reusing rate of waste water. (Xiao Xingxuan 1993)

6 CONCLUSIONS

In iron and steel industry, the process of iron and steel smelting produced a large amount of waste water and different kinds of waste water from different smelting steps. Due to the different technologies and methods were used, the waste water of iron and steel industry contents are different. The answer for the first research question in this thesis is: the major pollutants in the waste water which are produced by the process of iron and steel smelting are inorganic suspended solids, usually short for SS, heavy metals, oil and grease and acidic compounds.

Metallurgical industry includes two types of technologies, which are ferrous metallurgy (iron and steel) and non-ferrous metallurgy (light and heavy metals). In ferrous metallurgy, mainly two smelting methods are used, which are long-process, combined method (BOF method), and short-process, electric arc furnace (EAF) method. At present, most iron and steel industries use the BOF-method, the general process of the BOF method is: iron smelting, steel smelting, secondary metallurgy and continuous casting.

Any kinds of metallurgical methods produce a large amount of waste, and generate different kinds of waste gases or liquids such as smoke, dust and waste water. In the process of steel smelting by basic oxygen furnace (BOF) system, the waste water mainly comes from oxygen top-blown converter (BOF) waste water, continues casting machine waste water, and converter steel slag cooling waste water. All of above waste water have different characteristics and treatment methods.

The gas which is produced by the process steel smelting by BOF system is called converter gas, and there are two steps to deal with the converter gas. First, reduce the temperate of the converter gas to a certain temperature scope, and then purify the converter gas, which means remove the dust in the converter gas. The purpose of converter gas treatment is not only for protecting the environment by reducing the amount of pollutants in the released gas but also for collecting the converter gas for reuse. The converter gas floated through two stages venturi scrubbers for purifying the dust, after that, the converter gas can be collected and reused as the energy source, or sent to gas stations. These two steps of converter gas treatment will produce two kinds of waste water.

To answer the second research question, there are two technological systems are used in steel smelting plants. One is wet-type purifying method, which is known as the OG system, the other is dry-type purifying method, which is known as the LT system. The OG system is mainly applied in most steel smelting plants, because the OGs system is safer than the LT system.

To answer the last research question, which is how the OG system deals with the converter gas and waste water which are produced from the BOF steel smelting. First step will produce cooling waste water which is used for cooling high temperature converter gas; second step will produce purifying waste water which is used for removal of dust from the converter gas. Cooling waste water is much easier to handle, because the cooling water has no direct contact with the converter gas. In the OG cooling system, it can be reused without any special treatments but only reduce the temperature of the cooling water. Purifying waste water is more difficult to handle, because the purifying water has direct contact with converter gas. Hence, the purifying waste water contains a large amount of dust. The purpose of purifying waste water treatment is reuse. There are three technologies in this treatment, the removal of suspended solid, the stability of the water and the dehydration and reusing of sludge. Forced precipitation is applied in the removal of suspended solid; it is more effective than natural precipitation. Adding sodium carbonate is a good way for stabilizing the water. Two technologies were used in the dehydration and reusing of sludge, one is vacuum filter dehydrating technology, but this technology has a bad performance of dehydration, it is not used that much. The other one is pressure filter technology, it gives a more ideal performance of dehydration, it is highly applied by most steel smelting plants, but it is more expensive to operate.

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