



## Petrochemical Wastewater Characteristic Properties And Technologies

All of the following acidic water salinity, are tested and measured according to the national standard laboratory method. Due to ammonium salts' property of easy to volatile, the ammonium sulfide convert to ammonium hydrogen sulfide. In the laboratory measurement, the final accounts of salinity will be the total amount of ammonium hydrogen sulfide plus the acidic water salinity.

### 1. Acidic Water

Twelve types of acidic water from each plant area: Western zone CDU tower dehydration, Acidic water of catalyzing section, Acidic water of No.1 coking unit, Acidic water of No.2 coking unit, Acidic water of No.1 hydrogenation unit, Acidic water of No.2 hydrogenation unit, Acidic water of diesel restructuring unit, Eastern zone CDU tower dehydration, Acidic water of heavy catalyzing section, Acidic water of gas separator unit, Acidic water of gasoline hydrogenation unit, Acidic water of reforming unit.

#### Objective:

Each plant area has produced acidic water, all the acidic water will enter through stripping process (steamed ammonia desulfurization), then into the waste treatment plant. The cost of processing wastewater stripping is too high. In order to lower down the processing cost, processing the wastewater through diversion. Separate out the processing wastewater by concentration. By-product can be extracted from the high concentration of wastewater. After that, the remaining part of the wastewater can enter through stripping process. **Since the amount of acidic water has been reduced through diversion, the cost of stripping process will be lower down. The COD index of the water will also be reduced (The COD requirements is less than 2500 mg/L, sulfide is less than 50 mg/L, phenol is less than 250 mg/L. The COD requirement to discharge wastewater to efflux river is less than 60 mg/L, ammonia is less than 10 mg/L, sulfides less than 1 mg/L, phenol is less than 0.5 mg/L).** After that, base on the ammonia, sulfides, and COD concentration of acidic water level, the wastewater is divided into the following units:

#### (1) High concentration of acidic water

Ammonia, sulfides higher than 20000 mg/L, or COD higher than 30000 mg/L is defined as high concentration of acidic water (including acidic water of hydrogenation unit in refining No.4 workshop, acidic water of hydrogenation unit in refining No.7 workshop, washing water of gas separator section, acidic water of reforming unit), in total of about 20 square/ hour.



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Properties	Workshop	System	Drainage	Petroleum type	Ammonia mg/L	Sulfide mg/L	Volatile phenol mg/L	COD mg/L	Salinity	final accounts of salinity	Flow rate m3/h	Note
	High concentration of acidic water	Refining No.4	Hydrogenation unit	Acidic water delivery line	61	20000-50000	25000	Below 50	30000-70000	96	40096	8-11
Refining No.6		Gas separator unit	Washing water No.1	69	10863.2	41.48	97.4	53480	270	336.368	2-4	
			Washing water No.2		6757.89	82	11.27	450018			Acidic water line	
Refining No.7		Hydrogenation unit	Hydrogenation No.1	72		31258	123	62276	1405	51417.8	2-4	
			Hydrogenation No.2	92	17000	20000	200-533	30000	16	32016	8-10	
Chemical factory No.3		Reforming unit	V103	44	20863.2	9871.67	0.85	19421	52	15846.67	0.05	
	V105		31605.3		23808.16	1.91	48872	38093.06		Acidic water line		

The chart above shows that: High concentrations of acidic water is generally hydrogenated (also pre-hydrogenation reforming on part).

## (2) Low concentration of acidic water ( Except acid water of coking unit & 17 tons of CDU tower dehydration from a new project)

Low concentration of acidic water is other wastewater in stripping processing (ammonia and sulfides higher than 200, COD higher than 6000), included CDU tower dehydration of No.1 and No.5 refining workshop, acidic water of No.1 and No.2 coking unit (haven't blending during the high phenol residue), acid water of No.1 and No.2 catalyzing section, and acidic water of gasoline hydrogenation unit.

Workshop	System	Drainage	Ammonia mg/L	Sulfide mg/L	Volatile phenol mg/L	COD mg/L	Salinity	final accounts of salinity	Flow rate m3/h
Refining No.1	Atmospheric	Tower dehydration	50-200	86.493	600-1400	6000-14000	335	472.85	2-5
									Acidic water line
Refining No.2	Catalyzing	Acidic water tank	3743	2562.74	1086	12215		4084.37	13-16
Refining No.3	Coking	No.2 coking	6487.88	5381.771	188	24349	120	8697.20	12-15



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Refining No.5	CDU	Tower dehydration	100-200	99.55	400-1500	6000-15000	616	774.66	3-7
									Acidic water line
Refining No.6	Heavy catalyzing	Heavy catalyzing	1500-4000	2100	500-1400	6000-18000	600	3946.88	17-22
									Acidic water line
Refining No.8	gasoline hydrogenation	V301	5942.42	5573.977	206	14783		8883.53	Very little
		V202	1609.09	1473.58	566	7826		2348.52	1.5 square/day

Generally, the wastewater indexes of CDU tower dehydration, acidic water of catalyzing section, and acidic water of coking unit are very low. However, the volume flow rate are quite large, at about 66 square per hour.

## 2. Directly into the wastewater treatment plant

### (1) High concentration of acidic water

Among all types of wastewater which are directly discharged into the wastewater treatment plant, electric dewatering has the highest indexes of containing salinity from laboratory tests. (Salinity of the following data need to multiplied by two, water injection will be reduced later.)

Low concentration of wastewater	Workshop	System	Drainage	Petroleum type	Ammonia mg/L	Sulfide mg/L	Volatile phenol mg/L	COD mg/L	Salinity	final accounts of salinity	Flow rate m3/h	Note
	Refining No.1	CDU	Electric dewatering	38	30-200	25.627	544	1500-6500	1030	1071.03	12-16	Directly discharge after winze processing (the flow rate can be controlled at 6-10 square per hour later)
											Winze	
Refining No.5	CDU	Electric dewatering	75	55-120	82.96	250-450	3000-7000	1400	1532.736	Winze 5-20	The flow rate can be controlled later	

### (2) Low concentration of wastewater

Circulating water discharge: currently, the company has total of three cooling tower, but the wastewater discharge is not continuous. Therefore, the company has a new project to build an additional



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cooling tower. The average daily circulating water emissions of about 1000 square directly discharge to efflux river when the wastewater index are qualified to discharge directly. For the wastewater that unqualified to directly, it need to be sent to the wastewater treatment plant. The following indexes are from the wastewater that haven't discharged, and mostly unqualified to directly discharge. The emissions salt content in 2000-3000 mg/L.

Circulating water	Workshop	Petroleum type	Ammonia mg/L	Sulfide mg/L	COD mg/L	Salinity	PH	Concentration multiple
	Refining No.5	0	0.28	0	< 30	1416	7.86	2
	Refining No.7	0	0.11	0	46.4	1018	8.41	1.3
	Refining No.8	0.6	0.39	0	101	1275	7.39	2

### 3. High Salt Content Water (Salinity content of 2016 assessment is 1600 mg/l, require to reduce below 1000 mg/l)

#### (1) Existing System Device

The existing device is the alkaline residue treatment device. It is for high salt content water treatment. The indexes are: average volatile phenol is 650 mg/L, minimum volatile phenol is 170 mg/L, maximum volatile phenol is 1600 mg/L; average COD is 30000 mg/L, minimum COD is 20000 mg/L, maximum COD is 58000 mg/L; sulfide below 10 mg/L; salt content is 8%-16%. The device working intermittently. the starting treatment capacity is 0.8-1.5 square per hour. The wastewater has high salt content (mainly sodium or sodium sulfite, etc.). This is a urgent problem that the company need to solve.

#### Softening water from demineralized system

Categories	Full capacity of water t/h	Salt content	COD	NH4-N
Reverse osmosis concentrate water	100	5080 mg/L	< 30 mg/L	< 1 mg/L
Ion exchange regeneration wastewater	7	Higher than 5080 mg/L	400 mg/L	5 mg/L

#### (2) New project of high salinity wastewater:

**No.1) In the alkane dehydrogenation project, the indexes of waste lye from the exhaust gas treatment system:** salt content is 10-12 wt% (consisting of NaCl, Na<sub>2</sub>SO<sub>4</sub>); PH is 7-8. This is the most difficult and important part to solve. It is because the salt content is 10%-12%, and high sodium chloride content (up to 7%-8%). This part of water cannot be directly sent to the wastewater treatment plant, the volume flow rate of wastewater can up to 0.23 m<sup>3</sup>/h (intermittent emissions), daily average is 1.5-2 square/day.



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**No.2) Saline wastewater generated from butyl rubber bromine recovery.** The indexes of this wastewater are: flow rate is 30.5 m<sup>3</sup>/h; PH is 7-8; temperature is 45 °C; density is 1005 kg/m. Components: bromide (NaBr/CaBr<sub>2</sub>) is less than 300 ppm wt; chloride (NaCl/CaCl<sub>2</sub>) maximum is 3800 ppm wt; sulfate is less than 1500 ppm wt; hexane and other hydrocarbons are less than 100 ppm wt; stearate is less than 80 ppm wt; rubber power is less than 50 ppm wt; alky phenol is less than 10 ppm wt.

**No.3) Butyl rubber thermal oxidizer wastewater.** According to the thermal oxidation furnace technology package, the indexes of this wastewater are: flow rate is about 400-1000 kg/h. Components: BOD is less than 20 mg/L; COD is less than 120 mg/L; NaCl is 41,279.35 mg/L; NaBr is 6,547.42 mg/L.

The above saline wastewater are the urgent problems that the company need to solve. Because of these two projects will start product in recent months. The No.1) waste lye from the exhaust gas treatment system, No.2) saline wastewater generated from butyl rubber bromine recovery, and No.3) butyl rubber thermal oxidizer wastewater are not in the same plant, it can be treated individually, or treated together through pipeline transportation. We are highly recommend to treat separately (No.2 and No.3 are generated from the same device).

High Salt Content Water	Workshop	System	Drainage	Petroleum type	Ammonia mg/L	Sulfide mg/L	Volatile phenol mg/L	COD mg/L	Salinity	final accounts of salinity	Flow rate m <sup>3</sup> /h	Note
	Chemical factory No.1	Alkaline residue treatment device	Effluent	Mainly sodium or sodium sulfite		1	650	30000	80000-160000		0.8-1.5	
	Chemical factory No.2	Alkane dehydrogenation	Waste lye from the exhaust gas treatment system	Consisting of NaCl, Na <sub>2</sub> SO <sub>4</sub> ; PH is 7-8. High sodium chloride content (up to 7%-8%)				100000-120000		1.5-2 square per day		
	Material factory No.1	Butyl rubber	Bromine recovery	bromide (NaBr/CaBr <sub>2</sub> ) < 300 ppm wt; chloride (NaCl/CaCl <sub>2</sub> ) max. 3800 ppm wt; sulfate < 1500 ppm wt; hexane and other hydrocarbons < 100 ppm wt; stearate < 80 ppm wt; rubber power < 50 ppm wt; alky phenol < 10 ppm wt				30.5 m <sup>3</sup> /h				
			Thermal oxidizer	Components: BOD < 20 mg/L; COD < 120 mg/L; NaCl: 41,279.35 mg/L; NaBr: 6,547.42 mg/L				0.4 m <sup>3</sup> /h				
	Demineralized system	Reverse osmosis concentrate water		Salt content: 5080				100 m <sup>3</sup> /h				
Ion exchange regeneration wastewater				5			400		7 m <sup>3</sup> /h			