Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2021

### 1. Basic descriptions of two processes

### 1) via "Sulphuric Acid Vacuum concentration"

> **Typical Process:** Concentrating waste acid from 20% ~ 60% or even lower to 70% ~ 75% by pre-vacuum concentration process; concentrating acid from 70% to 85% by intermediate vacuum concentration; concentrating acid from 85% to 96% ~ 97% by high concentration process.

**Concentration:** w 
$$(H_2SO_4)$$
 20%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$  70%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$  85%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$  95%

### Phase I pretreatment:

It can be operated at atmospheric pressure or in vacuum. Different materials and types of heaters can be used according to the concentration of waste acid and impurity characters. Multi-effect (or multi-stages) vacuum concentration will undoubtedly save energy, but because multi-effect vacuum concentration will increase the investment cost of equipment, generally it is not recommended to use more than three-effect pre-concentration processes.

Phase II Intermediate vacuum concentration of sulphuric acid: 
$$w(H_2SO_4)$$
 20%  $\rightarrow \rightarrow \rightarrow w(H_2SO_4)$  85%

Generally, it operates under the absolute pressure of 8  $^{\sim}$  10Kpa and the operating temperature is 150 $^{\sim}$ 180 $^{\circ}$ C. For the devices with high processing capacity, it can be divided into two or more stages to reach the final required product concentrations.

Phase III Highly concentrated: w 
$$(H_2SO_4)$$
 85%  $\rightarrow \rightarrow \rightarrow w$   $(H_2SO_4)$  95%

The main equipment is metal tantalum, which is expensive. Steam consumption is huge during this process.

### ➤ About our task:

For the feed w ( $H_2SO_4$ ) 45%, theoretically, it is possible to be concentrated to various concentrations of acid in the range of 45% ~ 95%.

### 2) via "Spent sulphuric acid regeneration (SAR) process"

Process: thermal decomposition(Fuel must be added)→→gas clealing→→ dring&absorbtion→→converte

**Concentration:** w  $(H_2SO_4)$  60%  $\rightarrow \rightarrow \rightarrow w$   $(H_2SO_4)$  98%

Generally, the feed concentration should be w  $(H_2SO_4) > 60\%$ , because a large amount of water and air are brought into the combustion process. If the feed concentration is low, the heat balance of the conversion process will be affected. At the same time, if the water content is too high, the water balance in the dry suction section will be unbalanced.

### ➤ About our task:

The feed with 45% concentration of (H2SO4) appears to be low in concentration by the above mentioned SAR method and may be necessary to be concentrated first. Then use SAR process for further concentration and purification.

 $w (H_2SO_4) 45\% \rightarrow w (H_2SO_4) 65\% \rightarrow w (H_2SO_4) 75\% [w (H_2SO_4) 85\%, w (H_2SO_4) 95\%]$ 

Tab.1 Comparison of two processes:

comparative content	two processes				
comparative content	Sulphuric Acid vacuum Concentration	SAR			
Impurity content in waste acid	It is more suitable for waste acid with low impurity content. It is suggested that it is suitable for small amount of acid and low impurity content.	Using calciner to incinerate and electrostatic precipitation to remove burning dust, no matter how much impurity content in waste acid, the process can be used to treat the acid to reach high quality acid and it can be used in a wide range.			
Final product	Only sulphuric acid with a concentration of less than 98% can be produced, because 98% of the sulphuric acid is mixed with water during concentration, and only 98% can be achieved regardless of any measures taken. When the waste acid is concentrated, the solid impurities cannot be removed, but the water and volatile organic compounds are evaporated. The concentrated waste acid can only be reused by this product. Due to the recycling of concentrated waste acid, the pipeline is easy to be blocked after a long time, and acid sludge is easy to deposit at the bottom of the acid storage tank.	Different concentrations of waste acid can be produced. Similar to sulphur burning sulphuric acid, the quality of sulphuric acid produced could reach the national standard.			
equipment investment	The use of tantalum material in the acid evaporating tower, with enamel glass lining in the washing tower, and the investment of the two equipment are relatively high.	The processes from calciner to transformation, and dust removal is gas flow. The equipment volume and pipe size are large, the occupied area (or footprint) is large, and the equipment investment is large.			

	Daily maintenance of equipment	Vacuum concentration of waste acid is easy to leak under the condition of unstable temperature control and sharp change of temperature due to the use of some glass equipment pipes.	
	industrial wastes management	It mainly deals with acidic wastewater produced by condensation and acidic wastewater from vacuum pump.	Control the content of sulfur dioxide in waste gas, treat or use acid wastewater, and waste residue from electrostatic precipitator.
operational cost	Site environment and staffing	Depending on the size of the device, several full-time staff members are required.	The installation site is neat and clean, and the labor intensity of workers is not heavy.
Consumption of waste aci treatment		Steam or heat transfer oil is needed to vaporize water under vacuum condition.	A large amount of natural gas is needed. The calciner temperature is controlled at about 1000 $^{\circ}\mathrm{C}$ , and the water in the waste acid is vaporized.
	Other consumption	Waste acid, low pressure steam, electricity, by-product medical deoxidizing water, circulating water, analysis costs, medical depreciation, personnel wages, management costs	•

## 2. investigation of industrial waste acid treatment plant

# Tab.2 Concentration of industrial waste acids from different sources and their usual treatment processes

Various kinds of waste acid from	Waste acid concentration	Treatment process
different industrial processes		
Titanium dioxide waste acid	w (H <sub>2</sub> SO <sub>4</sub> ) 19%~23%	concentration
Aromatics nitrification waste acid	w (H <sub>2</sub> SO <sub>4</sub> ) 60%~70%	concentration
Dyestuff waste asid	w (H <sub>2</sub> SO <sub>4</sub> ) 10%~50%	Partly neutralization
Dyestuff waste acid		"or "concentration
Charles and a second	w (H <sub>2</sub> SO <sub>4</sub> ) 5%~10%	Recycling→FeSO4
Steel cleaning waste acid		$\llbracket \operatorname{Fe}_2(\operatorname{SO}_4)_3 \rrbracket$ n
Alkylation waste acid	w (H <sub>2</sub> SO <sub>4</sub> ) 85%~90%	regeneration (SAR)
MMA	w (H <sub>2</sub> SO <sub>4</sub> ) 40%、	concentration + regeneration
IVIIVIA	w【(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 】35%	(SAR)
Hydrofluoric acid drying waste acid	w (H <sub>2</sub> SO <sub>4</sub> ) 75%~85%	concentration
Chlor alkali waste acid	w (H <sub>2</sub> SO <sub>4</sub> ) 75%~80%	concentration "or" Air lift

	w (H <sub>2</sub> SO <sub>4</sub> ) 80%~90%	concentration "or"
Acetylene purifying waste acid		regeneration (SAR) "or"
		neutralization

Tab.3 operational cost of Sulphuric Acid Concentration (45%→→→96%)
(A device in Nanjing,china)

	unit consumption		Unit Price		Unit cost
Sulphuric acid 45%	2155	kg/t			(yuan/t)
Alkali (in kind)	180	kg/t	550	yuan/1000kg	99
Qing River water	200	kg/t	0.85	yuan/kg	170
circulating water	100	t/t	0.18	yuan/t	18
electric	69	kWh/t	0.65	yuan/kWh	44.85
Medium pressure steam	0.45	t/t	150	yuan/t	67.5
1.1MPa	1.2	t/t	140	yuan/t	168
Cost analysis					3
maintenance costs					10
Depreciation of equipment					20
Personnel wages					28.7
Management cost	_				10
operational cost					639.05

The vacuum concentration process needs two stages of enrichment, from 45% to 65% or 65% to 96%. The operational cost is about 600 yuan / ton (including depreciation).

Tab.4 operational cost of SAR(45%→→→96%) (A device in Nanjing, China)

		unit raw material consumption		Unit Price		Unit cost (yuan/t)
waste acid	45.00%	2155	kg/t			
Low pressure steam	0.8MPa	80	kg/t	130	yuan/1000kg	10.4
electric		95	kWh/t	0.65	yuan/kWh	61.75
By-product medium pressure steam	3.2MPa	-800	kg/t	150	yuan/1000kg	-120
Qingjiang River water		500	kg/t	0.85	yuan/1000kg	0.425
De-oxygen water		1160	kg/t	24	yuan/1000kg	27.84
circulating water		82000	kg/t	0.18	yuan/1000kg	14.76
Natural gas		230	Nm3/t	2.8	yuan/Nm3	644
Cost analysis						3
maintenance costs						3
Depreciation of equipment						40

Personnel wages			28.7
Management cost			10
operational cost			723.875

The operational cost of waste acid regeneration process is about 1000 yuan / ton.

The investigation of the industrial waste acid treatment plant has found that the source of waste acid, the type of impurity content, the initial concentration of waste acid, the concentration of finished acid, the amount of treatment, the steam used, the combustion gas and so on are the factors affecting the process combination, investment and operational cost of the treatment plant. Therefore, it is difficult to collect enough data from the completed projects in line with our task requirements.

In the following work, I intend to set the preconditions for a certain type of waste acid with a starting concentration of 45% w ( $H_2SO_4$ ), daily treatment amount, steam, and burning gas (calorific value), and ask experts to give rough estimations based on personal experience of different final sulphuric acid concentrations, investment and operating costs.

# 3. Waste sulfuric acid treatment and vacuum concentration process and its operational cost and investment analysis

Setting up the process condition of waste sulfuric acid concentration, analyzing different final sulfuric acid concentration, its investment and operational cost

### 1) cost estimation of waste sulfuric acid vacuum concentration process

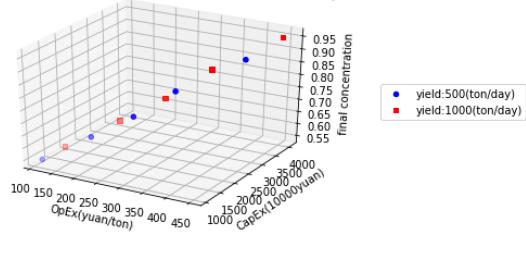
Tab.5 cost estimation of waste sulfuric acid vacuum concentration process

Primary	final	yield	СарЕх	ОрЕх	Domonico
concentration	concentration	(ton / day)	(10000 yuan)	(yuan / ton)	Remarks
450/	EE0/	500	1070	114.3	
45%	55%	1000	1800	112	
450/	CE0/	500	1400	202.5	
45%	65%	1000	2350	200	
450/	750/	500	1550	286	
45%	75%	1000	2630	283	
450/	0.50/	500	1870	354.6	
45% 85%	85%	1000	3170	350	
45%	95%	500	2670	450	

|--|

### 3Dgraph:

cost estimation of waste sulfuric acid vacuum concentration process



### 2) cost estimation of Spent sulphuric acid regeneration (SAR) process

The feed with 45% concentration of (H<sub>2</sub>SO<sub>4</sub>) appears to be low in concentration by Spent sulphuric acid regeneration (SAR) process method and can be concentrated first, then use SAR mode.

Because of it's high investment cost, professionals give the following suggestions and estimate the related costs for our task,.

w  $(H_2SO_4)$  45%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$  65% using waste acid concentration process; w  $(H_2SO_4)$  45%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$  75% using waste acid concentration process; w  $(H_2SO_4)$  45%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$  85% using two stage concentration process. w  $(H_2SO_4)$ 45%  $\rightarrow \rightarrow$  w  $(H_2SO_4)$ 95% using two stage concentration and regeneration process(SAR)

Tab.6 cost estimation of spent acid regeneration (SAR)processes

Primary concentration	final concentration	yield (ton / day)	CapEx (10000 yuan)	OpEx (yuan / ton)	备注
45%	6E0/	500	1441	215	vacuum
45%	65%	1000	2420	212	concentration
45%	75%	500	1610	300	vacuum
45%	75%	1000	2720	297	concentration
45%	85%	500	1970	364.6	2 stage

		1000	3320	358	vacuum concentration
		500	3600	750	2 stage
	5% 95%		6070		vacuum
45%		95%		745	concentration
	1000	6070	745	+ regeneration	
				(SAR)	

### 3Dgraph:

