

# Performance Evolution of Zero Effluent Discharge System for H-Acid Manufacturing Unit

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**ABSTRACT:** H-Acid (1-Amino, 8-Naphtol, 3-6 disulphonic acid) is a dye intermediate chemical, used as a coupler/ reactant in manufacturing of dyes. It is mostly manufactured by Small and Medium-sized entrepreneurs (SMEs) with a production capacity between 10 to 100 tonnes per month. H-acid plants, are being promoted in India as a potential foreign exchange earners. These plants generates highly concentrate acidic effluent stream in the volume of 22-24 liters / kg of product, having High COD and TDS values as mother liquor. The mother liquor waste water generated is passed through crystallizer to recover Glauber salt that is reused in H-acid manufacturing and acidic waste water will be neutralized. The neutralized effluent is passed through the multiple effect evaporator, to condensate at 10 litres/kg, which is reused back in the process for hot water wash /cooling tower. The concentrate mother liquor having specific gravity 1.3-1.35, is incinerated. In addition, the presence of toxic naphthalene-based dye intermediates in the wastewater made it non-biodegradable. The present system results in recovery of Glauber salt, reduction of salt in wastewater to smoothen the MEE operation and reuse of condensate water from MEE reducing the water requirement.

**KEYWORDS:** Chemical Oxygen Demand (C.O.D.), Reuse, Recycle, Recovery, Evaporation, Molecular Weight (M.W.), Mother Liquor (M.L.)

## I. INTRODUCTION

H-Acid is a dye intermediate chemical, used as a coupler/ reactant in manufacturing of dyes. The IUPAC product name of commercially known dye intermediate as H-Acid is 1-Amino 8-Naphtol 3,6-DiSulphonic Acid[1], having molecular weight of 319 and its sodium salt is 342. Amino 3, 6, 8-trisulphonic acid of sodium salt is not isolated in acidic media unless it is required for sale. Commercially this is known as Koch Acid. Total quantity of H-Acid manufactured throughout India doesn't exceed 3000 TPM. Out of 3000 TPM about 2000 TPM of H-Acid is manufactured in Gujarat State. The above product is manufactured from Naphthalene, a byproduct of steel industries & crude petroleum. The purity of Naphthalene is varying from 90-99.5% on HPLC / Gas Chromatographic analysis. It is preferable to use pure Naphthalene to save unwanted different chemicals for different reactions at different stages. The saving of chemicals will reduce the pollution load at the end of the reaction. Usually the product formation requires about 12 days. The theoretical conversion rate of Naphthalene to H-Acid is 2.49, but in practice its formation is 1.00-1.0. In actual production technology, hardly 40% of H-Acid is converted from Naphthalene. Due to the above reason the characteristic of wastewater formed during final stage is difficult to degrade in simple compounds through conventional processes. Due to this reason only it is presumed that the zero discharge of effluent is required to be achieved through different methodologies. The performance analysis of the different systems and processes are required to be checked to achieve real zero discharge of effluent generated in the manufacturing of H-Acid.

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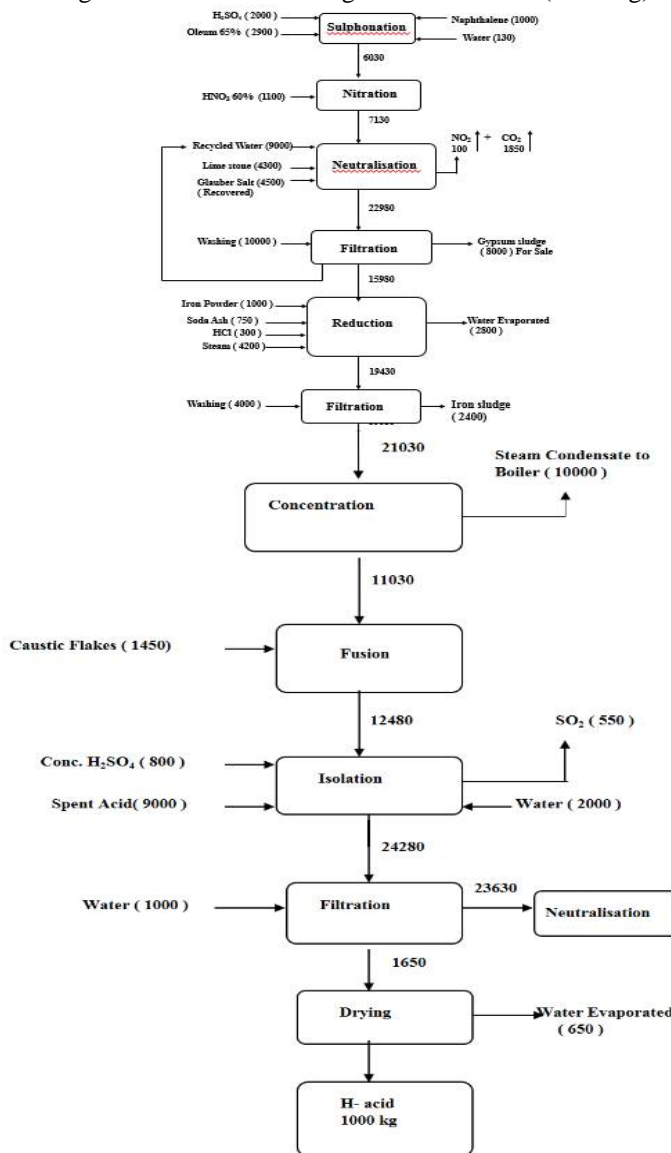
## II. MANUFACTURING PROCESS OF H-ACID

In actual production technology, hardly 40% of H-Acid is converted from Naphthalene. The process stage wise Raw material conversion [2] as per table:1 and Mass Balance Diagram as per Figure:1

Table: 1 Stage wise Raw Material Conversion

Sr. No	Process Stage	Conversion
1.	Sulpho-nation	78 % of Naphthalene to 3,6,8-Tri Sulphonic Acid
2.	Nitration	92 % of 3,6,8-Tri Sulphonic Acid to 1-Nitro 3,6,8-Trisulphonic Acid
3.	Neutrali-zation	98 % of 1-Nitro 3,6,8-Tri Sulphonic Acid to 1-Nitro 3,6,8-Sodium Salt of Naphthalene Tri Sulphonic Acid
4.	Gypsum Filtration	99.5 % of 1-Nitro 3,6,8-Sodium Salt of Naphthalene Tri Sulphonic Acid
5.	Reduc-tion	97 % of 1-Nitro 3,6,8-Sodium Salt of Naphthalene Tri Sulphonic Acid to 1-Nitro 3,6,8-Naphthalene Tri Sulphonic Acid (Koch Acid)
6.	Alkali Fusion	65 % of Koch Acid to 1-Amino 3,6- Naphthalene Disulphonic Acid of Sodium Salt
7.	Isolation	99.5 % of 1- Amino 3,6- Naphthalene Disulphonic Acid of Sodium Salt
8.	Filtration	96 % of 1- Amino 3,6- Naphthalene Disulphonic Acid of Sodium Salt
9.	Centri-fuge	98.5 % of 1- Amino 3,6- Naphthalene Disulphonic Acid of Sodium Salt
10.	Drying	97 % of 1- Amino 3,6- Naphthalene Disulphonic Acid of Sodium Salt

Figure:1 Mass Balance Diagram for H-Acid (1000 Kg)



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### III. BRIEF DESCRIPTION ABOUT ETP AND CHARACTERISTICS OF WASTEWATER

An Effluent Treatment Plant (ETP) is a unit plant, where various physical, biological and chemical processes are used to change the properties of the waste water by removing harmful substances in order to turn it into a type of water that can be safely discharged into the environment. Table 2 shows details of ETP plant unit from which this data is collected and Figure:2 shows total effluent (wastewater) generated per day. The wastewater coming out of H-Acid industries have very high toxicity as well as environmental degradation potential [3],[4]. Wastewater is characterized in terms of its physical, chemical and biological composition. The principal physical properties and the chemical and biological constitution of wastewater are reported in Table 3.

Figure:2 Water Balance Diagram

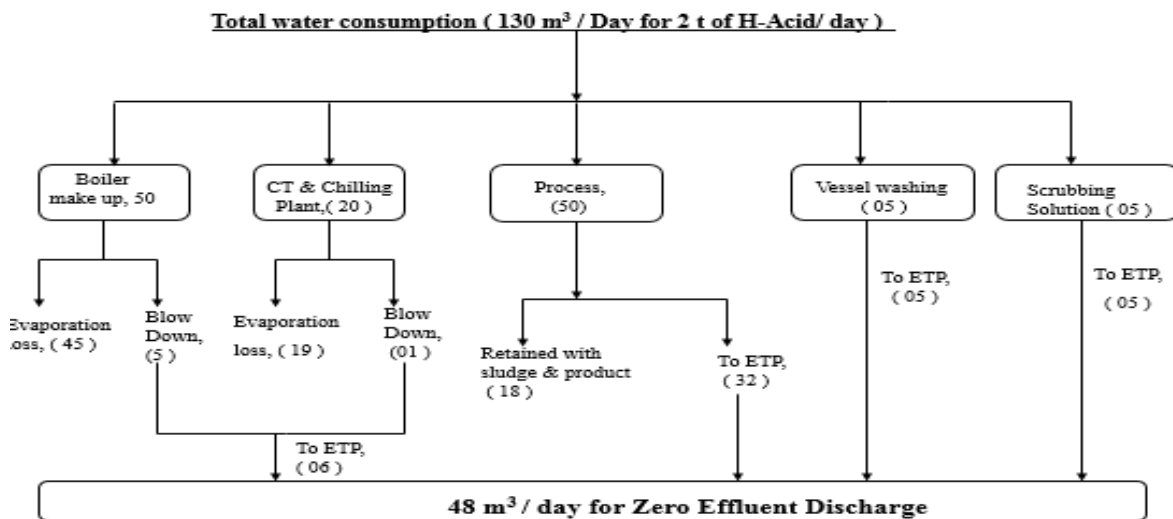


Table :2 ETP Units

Sr. No.	Name of Unit	Dimension in meter			No. Of unit
		Length	Width	Height	
1	Collection tank	3.0	3.0	4.0	1
2	Neutralization tank	3.0	3.0	4.0	1
3	Filter press (48 plates)	---	---	---	1
4	Holding tank	10.0	10.0	3.0	1
5	M.S. Holding tank (20 cu.m. )	---	---	---	2
6	Four effect Evaporator capacity (5000 l/hr)	---	---	---	1
7	Incinerator capacity (6000 l/hr)	---	---	---	01

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Table : 3 The Characteristics of Effluent  
(all parameters are measure in mg/L except pH)

Experiment done as per standard producer.

Sr No.	Parameter	ML from Isolation	After Crystallization	Neutralization tank	After 4th pass Evaporator
1	PH	0.85-0.89	0.85 -0.89	6.80-7.90	6.90 –7.80
2	TS	371100- 385000	100000 - 112000	205000 - 228000	370000 - 382000
3	TSS	1000-1500	1500-2500	600-700	700-800
4	TDS	370000-383500	98000-110000	186000-205000	325000-370000
5	Acidity	57500 - 58000	60000 – 62000	----	----
6	Sodium	112000 - 118300	66700 - 70200	54000 - 55500	138700 - 147500
7	Potassium	160 - 180	150 -175	80 - 95	350 -400
8	COD	102900 – 129300	134450- 137900	82560 - 89100	180150 – 186900
9	BOD <sub>3</sub> at 27°C	33400- 34300	38400 - 39200	24650 - 26300	35800 - 36400
10	Oil and Grease	60-85	65-100	65-90	70-110

#### IV. METHODS TO ACHIEVE ZERO DISCHARGE NORMS FOR H- ACID

The detailed scientific study should be verified with the present installed equipments as under to achieve zero discharge of effluent:

1. Wastewater Strength reduction
  - a. Recovery of byproducts by use of Crystallizer.
2. Wastewater Volume reduction
  - a. Reduction in volume of wastewater by use of Multiple Effect Evaporator.
3. Complete Thermal Distraction.

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## 1. Wastewater Strength reduction

### a. BY-PRODUCT RECOVERY:

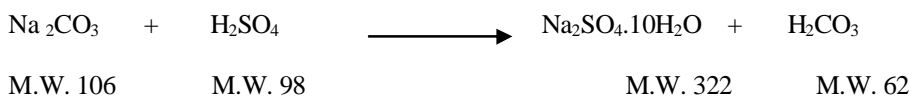
This is the utopian aspect of industrial –waste treatment, the one phase of the entire problem, which may lead to economic gain. All wastes contain by-products, the exhausted material used in the process. Since some wastes are very difficult to treat at low cost, it is advisable for the industrial management concerned to consider the possibility of the building a recovery plant which will produce a marketable by-product and at the same time solve a troublesome waste problem. From the wastewater of H-Acid, Gluaber salt (Sodium Sulphate) is recovered through Crystallizer. Due to recovery of Gluaber salt (G-salt) strength of wastewater is reduce also volume of wastewater is reduce.

#### CRYSTALLIZER:

Principle: Crystallization is the formation of solid particles within a homogeneous phase. It may occur as the formation of the solid particles in a vapor, as solidification from a liquid melt, or as crystallization from liquid solution.

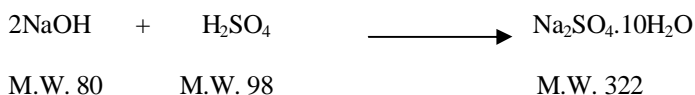
G-salt recovered by using Crystallizer: During manufacturing process of H-Acid Sodium Sulphate (G-Salt) is formed which is in soluble form. Sodium sulphate is recovered from Crystallizer which can be reused in process itself.

G-Salt ( Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O ) formed during reduction stage[1],[5],[6]:



$$\text{G-Salt formed} = \frac{322 \times 750}{106} = 2278 \text{ Kg/t of Hacid}$$

G-Salt (Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O) formed during Isolation stage:



$$\text{G-Salt formed} = \frac{322 \times 1450}{80} = 5836 \text{ Kg/t of H acid}$$

Total G-Salt formed = (2278 + 5836) = 8114Kg / t of H-Acid

G-Salt recovery is about 60%. So G-Salt recovered = 8114X 0.6 = 4868 Kg/ t of H-Acid

Volume of effluent 23600 Kg/ t of H-Acid & Sp.Gr.  $\cong$  1.2

So Volume of effluent = 23600 / 1.2 = 19667  $\cong$  19700 L / t of H-Acid

Volume reduction of effluent  $\cong$  4500 L due to recovery of G-Salt.

$\therefore$  Net acidic volume for treatment after recovery of G-Salt = 19700 – 4500 = 15200 L / t of H-Acid

## 2. Wastewater Volume reduction[7]:

To reduce the volume of wastewater to be incinerated, Multiple Effect Evaporator is used. The main benefit of evaporator is the reduction of wastewater and the condensation from the evaporator, which is used as boiler feed water. Detailed regarding Multiple Effect Evaporator is shown in Table:4.

- Procedure for measurement of Inlet Feed rate of liquid to Four effect evaporator: To measure the feed rate of wastewater a rod is dipped up to the bottom of cylindrical tank. Rod is wet upto liquid level this point is marked and measures the liquid level in the tank. Each hour same procedure is repeated to determine the difference in level (Table:5) [8]. Dimension of tank: 7.00 (m) length and 2.44 (m) Diameter.

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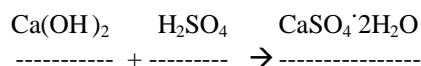
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- Procedure for measurement of Outlet Discharge rate of liquid from Four effect evaporator: To measure the outlet from four effect evaporator a 100 L capacity bucket is used. Total time required to fill bucket is find out by stopwatch and noted time (Table:5).
- The industry has installed incinerator of capacity about 6000 L / hr. So an attempt is find out actual incineration rate of incinerator. The data regarding incineration rate (Table 6) [8] and dimension of M.L. tank are mention below :

Dimension of M.L. tank:

Part-1 → 4.5 L(m) X 1.2 W(m) X 0.6 D(m), Part-2 → 3.4 L (m) X 1.2 W (m) X 1.7 D(m)

- **Hazardous (Solid waste generation)** [9],[10] The effluent has very low pH, the acidic effluent has to be neutralized to meet the standard set by G.P.C.B. for pH minimum as 6.5. For neutralization of wastewater about 850 Kg Hydrated lime is used which produces sludge in the form of gypsum. Hence, sludge generation in form of Gypsum will be as under [1],[5],[6]:



74                      98                      172

$$= \frac{172}{74} \times 850$$

$$= 1975 \text{ Kg Say } 2000 \text{ Kg/ t of H-Acid.}$$

**OR** 2100 Kg to 2200 Kg Wet Cake basis 5 % to 10 % Moisture.

Table : 4 Details regarding Four Effect Evaporator

Sr.No.	Characteristics	Details of Four effect
1	Installed capacity	5000 lit/hr of mother liquor
2	Operating parameters	
A	Feed rate	12500 lit/hr
B	Feed pH	7.00
C	Feed specific gravity	15 Bomi
D	Discharge sp. gravity	30 Bomi
E	Rated evapo ration rate	4700-5100 lit/hr
F	Working temperature	750 C

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Table : 5 Level Measurement in Feed Tank of Four Effect Evaporator

Sr. No.	Level in feed tank , (cm )	Difference in feed tank level,(cm)	Time interval, hr	Inlet flow, m <sup>3</sup> / hr	Out let flow, m <sup>3</sup> / hr	Volume reduction, (%)
1	195.2	-----	0	---	---	---
2	161.0	34.2	1.0	5.113	2.416	52.75
3	131.0	30.0	1.0	4.982	2.466	50.51
4	101.9	29.1	1.0	4.944	2.384	51.78
5	68.8	33.1	1.0	5.332	2.500	53.11

Table : 6 Measurement of level in M.L. tank for Incineration Rate

Sr. No.	Time (hour )	Level in ML tank,( m)		M.L. incinerated, L/ hr
		Difference of Level in part-1	Difference of Level in part-2	
1	1:00	0.320	0.731	4710
2	1:00	0.342	0.713	4756
3	1:00	0.301	0.752	4693
4	1:00	0.404	0.620	4712

Effluent Treatment Plant (ETP) operation cost comes around 21.23 INR per Kgs of H-acid. Here cost of incineration is the highest and cost of the four effect evaporator is low (Table 7). As per table 8, if we consume spent Sulphuric acid from the process itself, it will save the cost. If we use recovered G-salt than consumption of soda ash will be reduced, which will reduce the cost and will be more environment friendly. Coal consumption for incineration will be reduced because of multiple effect evaporators. Hence total savings is going to be increased due to above measures. During Incineration Air pollution is generated is controlled by providing scrubbing system to achieve norms of C..P.C.B [4], [11].

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Table : 07 Operating Cost of ETP / Kg Of H-ACID

Sr.No.	Particulars	Cost ( Rs.)
1	Neutralization of Acidic Wastewater (20000 L)	Rs.2.070
2	Cost of Crystallizer and Chilling Plant (12 hrs.)	Rs.2.798
3	Cost of Four Effect Evaporator (3 hrs.)	Rs.1.290
4	Cost of Incinerator (1.5 hrs.)	Rs.10.080
5	Cost of Sodium Hydroxides (NaOH) (for Scrubbing)	Rs.3.500
6.	Solid/ Hazardous waste disposal	Rs.1.500
	<b>TOTAL</b>	<b>Rs. 21.238</b>

Table : 08 Saving during treatment and incineration for 1ton of H-ACID

Sr. No	PARTICULARS	Total Saving (Rs)
1	<p>Sulphuric Acid required for Isolation stage is three tones. Cost of Sulphuric Acid is Rs. 3/ Kg.</p> <p>Spent Sulfuric acid is available at Zero Cost instead of Sulphuric acid which is used in Isolation sage.</p> <p>∴ Saving due to use of spent Sulphuric acid instead of Concentrated Sulphur acid : Rs. 3 / Kg. X 3000 Kg</p>	Rs.9000.00 / t of H-Acid
2	<p>Recovered G-Salt is used in Neutralization stage instead of Soda Ash. About 3 tones Soda ash will be saved. Cost of Soda ash : Rs.3.50/ Kg</p> <p>∴ Saving due to use of G-Salt instead of Soda ash Rs. 3.15 / Kg. X 3000 Kg.</p>	Rs. 9500.00 / t of H-Acid
3	<p>COAL saving due to the Volume reduces from 15000 lt. To 7500 lt. Through Four effect evaporator which reduced coal Consumption in the incinerator is about 1250 Kg. The cost of Coal is Rs. 8 / Kg .</p> <p>∴ Saving is Rs. 8/ Kg X 1250 Kg</p>	Rs.10000.00/ t of H-Acid
	Net saving in manufacturing of 1000 Kg of H-Acid = TOTAL OF 1+2+3	28500 Rs / 1000 Kg H-Acid
	Say saving is Rs. 28.500/Kg of H-acid against treatment cost of Rs.21.238/ Kg of H-acid including incineration, G.S. recovery and Secured land fill.	



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## V. CONCLUSION

Based on the detailed study carried out and details presented above following conclusion have been drawn:

1. Average quantity of wastewater generation is 24 KL/ T of H-acid.
2. The G-salt recovery reduces the volume of wastewater by 4500 L.
3. The wastewater volume reduction achieved in Four Effect Evaporator is 7500 L.
4. The incinerator operates at 78% efficiency as the incineration rate is determined is 4700L/hr against the rated capacity of 6000L/hr.
5. The operating cost of installed facilities to achieve Zero discharge works out to be Rs. 21.238/ Kg of H-acid.
6. The quantity of sludge generated to achieve Zero discharge is 2.1 T/ T of H-acid.

## REFERENCES

- [1] Norman Donaldson, The Chemistry and Technology of Naphthalene Compounds, Edward Arnold ( Publishers ) Ltd.
- [2] Warren L. McCabe, Julian C. Smith, Peter Harriott, Unit Operation of Chemical Engineering , Fifth Edition,1993, McGRAW –Hill, INC.
- [3] Nelson I. Nemerow, Industrial Water Pollution, Addison-Wesley Publishing Company.
- [4] [http://cpcb.nic.in/Industry-Specific-Standards/Effluent/DyeandDye\\_Inter\\_Indus.pdf](http://cpcb.nic.in/Industry-Specific-Standards/Effluent/DyeandDye_Inter_Indus.pdf).
- [5] Sawyer, Clair N., McCarty, Chemistry for Environmental Engineering, Fourth Edition, 2003.
- [6] B I Bhatt, S M Vora, Stoichiometry, Third Edition, 1996, Tata Mcgraw Hill, New Dehli
- [7] Trivedi R. K., " Low Cost and Energy Saving Technologies for Water and Wastewater Treatment"Journal of Industrial Pollution Control 23(2) (2007) pp 403-411.
- [8] <http://www.handymath.com/cgi-bin/circlevali25.cgi>
- [9] Charles A. Wents, Hazardous Waste Management, Second Edition,1995, McGREW- Hill, inc.
- [10] Connett, P., and Sheehan, B., "Citizens Agenda for Zero Waste: A North American Perspective," GRRN,October 2001
- [11] Noel De Nerves, Air Pollution Control Engineering, Tata Mcgraw Hill, New Dehli