ANNEXURE R4-24

BODAL CHEMICALS LTD.-Unit-VII
(GOVT. OF INDIA RECOGNISED EXPORT HOUSE)
Address : Block No. 795 To 803, 804, 807, 832, Vill : Dudhwada, Ta : Padra. Dist. Vadodara, Pin. 391 450, Gujarat (INDIA)
E-mail : unit7@bodal.com **Mobile #** 91-99099 50852-53-54-55, **Phone #** 02662-273801-803 **CIN #** L24110GJ1986PLC009003

ISOQAR QUALITY ASSURED ISO 9001

Ref # BCl-7/16-17/
Date: - 05/07/2016

To,

The Vadodara Enviro Channel Ltd.,
Plot # 304/1, 317 & 318
At & Post Dhanora
Dist.Vadodara

Kind Attn : Shri Satish Panchal (Managing Director)

Sub:- Permission to install online TOC Meter near to our Effluent Treatment Plant.

Dear sir,

With reference to above subject, we have installed online TOC meter near compound wall towards ECP Channel at present. Due to distance between TOC meter and ETP, our ETP operating peoples facing major problem for parameters re- confirmation with TOC meter's results. If TOC meter is installed near outlet line of effluent treatment plant, they can easily monitor all parameters with our ETP Lab results at the same time.

Furthermore, as you know sir, Reliance industries ltd had laid underground lines of gas and solvents parallels to VECL Channel. At present, we have installed TOC meter over their underground lines. Officials from Reliance industries have given verbal instruction to remove structure of TOC meter from where, present installation of TOC meter is done. So we decide to change place of installation from present to our ETP.

Sir, we request you to give us permission for this. Please do the needful.

Thanking you,

Yours Faithfully
For Bodal Chemicals Ltd (Unit-7)

Authorized signatory

6/7/16

True Copy

[redacted]

Bodal Chemicals Ltd.
COLOURS. INTEGRATION. INNOVATION.

To,
Managing Director,
Vadodara Enviro Channel Limited,
Plot No: 304/1, 317 & 318,
At and Post-Dhanora,
Dist: Vadodara-391 346.

Dt: 28/11/2016

Dear Sir,

Sub: Payment towards installation of Online Real Time Monitoring System.
Ref: Your Letter No: VECL/DHN/MD/637 Dt: 07/11/2016.

In receipt of your letter, please find attached here with a cheque worth of Rs3000000/-(Rupees Thirty Lacks) only bearing instrument No: 024 931 dt: 29/11/2016 towards installation of Online Real Time Monitoring System drawn at Union Bank of India, IFB-Branch, Ashram Road, Ahmedabad.

This payment is being made for and on behalf and consent with the management.

Thanking you.

Yours truly,
For: Bodal Chemicals Limited

Authorized Signatory

Encls: As above

30/11/2016

HEAD OFFICE:
Plot No. 123-124, Phase-1,
G.I.D.C, Vatva, Ahmedabad- 382 445.,
Gujarat, India.
Tel: +91 79 2583 5437
2583 4223, 25831684
Fax: +91 2583 5245, 25836052
E-mail: bodal@bodal.com

PLANT OFFICE:
UNIT - 7
Plot No. 804, Village : Dudhwada,
Ta. : Padra - 391450.
Tel: +91 99099 50852 - 853 - 854
02662 - 277801 / 802 / 803
Fax: +91 0266 2273804
E-mail: dyes7@bodal.com

www.bodal.com
CIN No. : L24110GJ1986PLC009003

यूनियन बैंक ऑफ इंडिया **Union Bank** of India

A/C PAYEE ONLY

आय एफबी अहमदाबाद गुजरात - ३८००१४
IFB Ahmedabad, Gujarat - 380 014.
IFS Code : UBIN0550353

Valid for 3 months from the date of issue

दिनांक Date 29-11-16
D D M M Y Y Y Y

Pay VADODARA ENVIRO CHANNEL LIMITED या धारक को **Or Bearer**

रुपये **Rupees** Thirty Lakh Only

अदा करें। ₹ ******30,00,000/-

खाता सं॰ A/c No. 503505010077011

चेक क्र Cheque No. 12024931

For BODAL CHEMICALS LTD.

AuthorisedSignatories
Please sign above

भारत की हमारी सभी शाखाओं में सममूल्य पर देय
PAYABLE AT PAR AT ALL OUR BRANCHES IN INDIA

Seshaasai (M) / CTS-2010 17-10-2016 CA 1336213

⑈024931⑈ 380026030⑆ 503512⑈ 29

True Copy

ANNEXURE R4-26

EMS FLOW METER DETAIL

SR.NO	PLANT	BEFORE 2018	2019	2020	2021	2022	TOTAL
		OLD					
1	H ACID PLANT	2	0	0	0	1	3
2	H ACID MEE PLANT	6				3	9
3	H ACID MEE PLANT PIPELINE STORAGE TANK	0	0	0	0	2	2
4	VS PLANT	2	0	0	0	4	6
5	VS MEE PLANT	4	0	0	0	2	6
6	VS MEE PLANT PIPELINE STORAGE TANK	0	0	0	0	2	2
7	BETA PLANT	1	0	0	0	2	3
8	DYES PLANT	0	0	0	0	4	4
9	ETP PLANT	6	0	0	0	2	8
10	ADVANT PLANT	9	0	0	0	3	12
11	ETP MEE PLANT	2	0	0	0	1	3
12	GROUND WATER PLANT	11	0	0	0	2	13
13	SPRAY DRAYER	0	0	0	0	1	1
	Total:	43	0	0	0	29	72

True Copy

ANNEXURE R4-27

THE ADEQUACY CERTIFICATE OF ENVIRONMENT MANAGEMENT SYSTEM

M/s Dharmsinh Desai University, Department of Civil Engineering is recognized by the GPCB, Gandhinagar under the Environmental Audit scheme introduced by the Gujarat High Court vide its Orders dtd. 20/12/96 & 13/3/97 and modified vide Order dtd. 16/9/99 as and Environmental auditor for the purpose of the auditing having carried out Environmental Audit of

a) M/S : **BODAL CHEMICALS LIMITED**
b) Located at : Block No: 804, Village-Dudhwada, Taluka-Padra, Dist : Vadodara (Guj)
c) Manufacturing products as under:

No.	Products	Quantity (MT/Month)
1.	H-Acid	150
2.	Vinyl Sulphone	200
3.	Acetanilide	150
A.	Ramazol Dyes such as Black mix, Black -5	500
B.	Reactive Dyes such as Reactive Red 195, Reactive Yellow 145	250
C.	Direct Dyes such as Acid Black 194, Acid Black 210 , Direct Black 22	250
4.	β-naphthol	500
By product		
1.	Glauber Salt (V.S. plant)	90
2.	Glauber Salt (H – Acid plant)	150
3.	Acetic Acid	35
4.	Gypsum Sludge	850

As per the directions of Hon. High Court in Environmental Audit Scheme and based on personal monitoring (collection of samples, analysis etc). We certify that the Environmental Management System provided by this industry for the products and capacity as stated above is adequate and efficacious to achieve the quality of effluents (Air + Wastewater + Solid waste) as specified/required Consent/Notifications by GPCB, Gandhinagar for following quantity of effluents.

a) Liquid effluent:

474 m^3/Day (Industrial)
475 m^3/Day (Industrial from Sulfur Product Division having CCA No. AWH: 75247)
8 m^3/Day (Sewage)

b) Solid Waste (Ash-ETP-Process & Iron):

Sr. No.	Type of Waste	Category & Schedule	Quantity (MT/m)	Method of Disposal
1.	Incineration Ash	37.2, Sch-I	85	Collection, Storage, Transportation & Disposal to NECL TSDF site
2.	Distillation residues	36.1, Sch-I	1.5-2	Collection, Storage, Transportation & Disposal to CHWI facility.
3.	Used Oil	5.1, Sch-I	100 L/Yr. (Max)	Collection, Storage, Transportation & Selling to recyclers authorized by CPCB
4.	Discarded containers / Liners	33.1, Sch-I	@ 17,000 nos.	Collection, Storage, Transportation & reused for disposal of waste storage to TSDF site.
5.	Process sludge from filtration & neutralization	26.1, Sch-I	1350	Collection, Storage, Transportation & Disposal to TSDF
6.	Iron Sludge	26.1, Sch – I	31.5	Disposal to authorized TSDF Site or sell out to authorized cement manufacturing unit.
7.	Spent Sulfuric Acid	26.3 , Sch – I	1400 – 1500	Captive consumed in H – Acid plant/ sell to actual users who obtained permission under Rule – 9
8.	Hydrochloric Acid 30 %	26.3, Sch – I	390	Sell to actual users who obtained permission under Rule – 9

In CCA Renewal ETP Sludge has been shifted in CCA of Appollo Dye Chem Pvt, Ltd., as they are operating our ETP Sludge and responsible for disposing the ETP Sludge.

c) Air Emission : Adequate/~~not adequate~~
Efficacious/~~not efficacious~~
(Flue gas stack as well as process stacks)

This certificate is valid for the audit period only. However, it is subject to automatic cancellation in case of any change in product profile/capacity, quality & quantity of effluent emission (Air + Water + Solid/Hazardous) and efficiency of EMS equipment.

This certificate forms part of Environmental Audit report.

Date: 09 JUN 2018
Place: Nadiad

For, BODAL CHEMICALS LIMITED
Director/Authorized Signatory

Signature of the Authorized Person

Name & Address of the Auditor:
Dharmsinh Desai University
Department of Civil Engineering
College Road,
Nadiad - 387 001.

Coordinator
Environmental Audit Cell

(Dr. H. M. Desai)
Vice Chancellor

Adequacy Certificate of Environmental Management System

The Environmental Engineering Laboratory, M. S. Patel Department of Civil Engineering, **Charotar University of Science & Technology**, **Changa** is recognized by the GPCB, Gandhinagar under the Environmental Audit Scheme introduced by the Hon'ble High Court Gujarat, vide its orders dated 20/12/1996 and 13/3/1997 and modified order dated 16/9/1999, as an environmental auditor for the purpose of the auditing, having carried out

Environmental audit of,

- M/s. Bodal Chemical Ltd.(Unit-VII)

- Located at: Plot NO.804, vill: DADHWADA,
Tal: Padra, Dist: Vadodara-394116
- Manufacturing products as under:

Sr. No.	Product Name	GPCB Production Limit as per CCA MT/Month
1	H-acid	150MT/Month
2	Vinyl Sulphone	200 MT/Month
3	Acetanilide	150 MT/Month
4	Crude Synthetic Organic Dyes	1000 MT/Month
	(A) Ramazol Dyes Such as - Black mix - Black 5	500 MT/Month
	(B) Reactive dyes such as - Reactive red 195 - Reactive yellow 145	250 MT/Month
	(C) Direct acid dyes such as - Acid black 194 - Acid black 210 - Direct black 22	250 MT/Month
5	Beta-Napthol	500 MT/Month
	BY PRODUCT	
	1. Glauber Salt (From VS plant)	90 MT/Month
	2. Glauber Salt (From H acid plant)	150 MT/Month
	3. Acetic Acid	35 MT/Month
	4. Gypsum Sludge	850 MT/Month

Having completed the environmental audit based on personal monitoring, and audit report, prepared as per the direction of the Hon'ble High Court in Environmental Audit Scheme, it is certified that the Environmental Management System (EMS) provided by this industry for the products manufactured and capacity as stated above is Adequate & Efficient to achieve the quality of effluents (Air + Wastewater + Solid Waste) as specified in consent/Notifications by GPCB, Gandhinagar for the following quantity of waste generation:

Liquid Effluent	Including Chemical Units	1. Industrial Effluent	474 KL/Day
		2. Domestic Wastewater (Sewage)	8 KL/Day
Solid Waste Solid Waste		1. Incineration Ash	As per the Consent
		2. Distillation Residues	
		3. Used Oil	
		4. Contaminated Discarded Containers/ Liners	
		5. Process sludge from filtration & neutralization	
		6. Iron sludge	
		7. Spent Sulphuric acid	
		8. HCL 30%	
Air Emissions Flue gas Stacks as well as process stacks		**Adequate**/~~not adequate,~~ **Efficacious**/~~not efficacious~~	

This certificate is valid for the audit report/ Audit Period only. However, it is subject to automatic cancellation in case of any change in product profile/capacity, quality and quantity of effluent emission (Air + Waste Water + Solid/Hazardous) and efficiency of EMS equipment.

This Certificate forms part of environmental audit report.

Name & Address of the Environmental Auditor

Environmental Engineering Laboratory, M. S. Patel Department of Civil Engineering,

Charotar University of Science & Technology,
CHARUSAT Campus, Changa, Dist.: Anand, State: Gujarat - 388 421

Signature of Environmental Auditor

Sr. No.	Name & Designation	Sign
1	**Mr. Gaurav V. Kapse** (Environmental Engineer)	
2	**Mr. Gaurav R. Patel** (Chemical Engineer)	
3	**Dr. Seema Amin** (Microbiologist)	
4	**Mr. Jinit R. Patel** (Chemist)	

Date: 28/06/2019

Place: Changa, Anand

For, BODAL CHEMICALS LIMITED
Director/Authorized Signatory

THE ADEQUACY CERTIFICATE OF ENVIRONMENT MANAGEMENT SYSTEM

M/s Dharmsinh Desai University, Department of Chemical Engineering is recognized by the GPCB, Gandhinagar under the Environmental Audit scheme introduced by the Gujarat High Court vide its Orders dtd. 20/12/96 & 13/3/97 and modified vide Order dtd. 16/9/99 as and Environmental auditor for the purpose of the auditing having carried out Environmental Audit of

a) M/S : **BODAL CHEMICALS LIMITED**
b) Located at : Block No: 804, Village-Dudhwada, Taluka-Padra, Dist : Vadodara (Guj)
c) Manufacturing products as under:

No.	**Products**	**Quantity (MT/Month)**
1.	H-Acid	150
2.	Vinyl Sulphone	300
3.	Acetanilide	650
4.	ASC Mass	500 (Captive 300)
5.	Reactive Black Dyes (Ramazol Dyes)	1250
6.	Reactive Red, Reactive Yellow & others	500
7.	Direct Acid Dyes	1250
8.	β-naphthol	500
9.	Cogeneration Power Plant	5 MW
By product		
1.	Glauber Salt (V.S. plant)	130
2.	Glauber Salt (H – Acid plant)	150
3.	Acetic Acid	51
4.	Gypsum Sludge	850

As per the directions of Hon. High Court in Environmental Audit Scheme and based on personal monitoring (collection of samples, analysis etc). We certify that the Environmental Management System provided by this industry for the products and capacity as stated above is adequate and efficacious to achieve the quality of effluents (Air + Wastewater + Solid waste) as specified/required Consent/Notifications by GPCB, Gandhinagar for following quantity of effluents.

a) Liquid effluent:

- 452 m3/day (427 m^3/day Industrial + 25 m^3/Day Domestic) ECP Channel + 230 m^3/Day high Conc. Effluent
- 475 m^3/Day (Industrial from Sulfur Product Division having CCA No. AWH: 75247), 8 m^3/Day (Sewage)

b) Solid Waste (Ash-ETP-Process & Iron):

Sr. No.	**Name of waste**	**Category No. as per HWM Rules, 2008**	**Quantity**	**Method of Disposal**
HAZARDOUS WASTE				
1	ETP Sludge	35.3 of Schedule I	400-425 MT/M	Included in CTO of Apollo Dye Chem.
2.	Process sludge from filtration and neutralization	26.1 of Schedule I	1350 MT/M	Collection, storage, transportation & Disposal to TSDF site or Sold to cement manufacturing units.
3	Iron sludge	26.1 of Schedule I	315 MT/M	Collection, Storage, Transportation & Disposal to TSDF site or Sold to cement manufacturing units.
5	Incineration /Spray Drying Ash	37.2 of Schedule I	245 Mt/M	Collection, Storage, Transportation & Disposal to TSDF site.
4	Distillation residues	36.1 of Schedule I	1.5 – 2 MT/M	Collection, Storage, Transportation & Disposal to CHWI facility
6	Used oil	5.1 of Schedule I	150 L/Y (Max)	Collection, storage and sold to registered recyclers.
7	Discarded containers / liners	33.1 of Schedule I	@17,000 nos. / M	Collection, storage and reused for disposal of waste storage to TSDF site.
8	Spent sulphuric acid	26.3 of Schedule I	2100-2300 MT/M	Captively consumed in H-Acid manufacturing and other
9	Hydrochloric acid	26.3 of Schedule I	810-975 Mt/M	It is reused as captive consumption for Dyes manufacturing.
NON – HAZARDOUS WASTE				
1	Fly Ash	--	@ 240 T/M	Collection, Storage, Transportation & reused in cement manufacturing industry, brick manufacturing industry.
2	Bottom Ash	--	@ 100 T/M	Collection, Storage, Transportation and reused for filling of low lying area, in brick manufacturing industry.

c) Air Emission : Adequate/~~not adequate~~
Efficacious/~~not efficacious~~
Refer Annexure - XVII

This certificate is valid for the audit period only. However, it is subject to automatic cancellation in case of any change in product profile/capacity, quality & quantity of effluents (Air + Water + Solid/Hazardous) and efficiency of EMS equipment.

This certificate forms part of Environmental Audit report.

Date: 01 JUL 2020
Place: **Nadiad**

Name & Address of the Auditor:
Dharmsinh Desai University,
College Road,
Nadiad – 387 001.

For, BODAL CHEMICALS LIMITED
Director/Authorized Signatory

Signature of the Authorized Person

Coordinator
Environmental Consultancy Cell

Adequacy Certificate of Environmental Management System

The Environmental Engineering Laboratory, M. S. Patel Department of Civil Engineering, **Charotar University of Science & Technology**, **Changa** is recognized by the GPCB, Gandhinagar under the Environmental Audit Scheme introduced by the Hon'ble High Court Gujarat, vide its orders dated 20/12/1996 and 13/3/1997 and modified order dated 16/9/1999, as an environmental auditor for the purpose of the auditing, having carried out

Environmental audit of,

- **M/s. Bodal Chemical Ltd.(Unit-VII)**
- **Located at: Plot NO.804, vill: DADHWADA,Tal: Padra, Dist: Vadodara-394116**
- **Manufacturing products as under:**

Sr. No.	Product Name	GPCB Production Limit as per CCA MT/Month
1	H-acid	150MT/Month
2	Beta Napthol	500 MT/Month
3	Acetanilide	650 MT/Month
4	Acetanilide ChloroSulphonated mass	500 MT/Month
5	Vinyl Sulphone (ACS Based)	300 MT/Month
6	Reactive red, Yellow and other	500 MT/Month
7	Reactive Black dyes(Ramazol dyes)	1250 MT/Month
8	Direct acid dyes	1250 MT/Month
9	Cogeneration Power Plant	5 MW
Total		**5200 MT/Month**
BY Product		
1	Glauber salt(from VS plant)	130 MT/Month
2	Glauber salt(from H-acid plant)	150 MT/Month
3	Acetic Acid	51 MT/Month
4	Gypsum Sludge	850 MT/Month

Having completed the environmental audit based on personal monitoring, and audit report, prepared as per the direction of the Hon'ble High Court in Environmental Audit Scheme, it is certified that the Environmental Management System (EMS) provided by this industry for the products manufactured and capacity as stated above is Adequate & Efficient to achieve the quality of effluents (Air + Wastewater + Solid Waste) as specified in consent/Notifications by GPCB, Gandhinagar for the following quantity of waste generation:

Liquid Effluent	Including Chemical Units	1. Industrial Effluent	452 KL/Day
		2. Domestic Wastewater (Sewage)	25 KL/Day
Solid Waste Solid Waste		1. Incineration Ash	As per the Consent
		2. Distillation Residues	
		3. Used Oil	
		4. Contaminated Discarded Containers/ Liners	
		5. Process sludge from filtration & neutralization	
		6. Iron sludge	
		7. Spent Sulphuric acid	
		8. HCL 30%	
Air Emissions Flue gas Stacks as well as process stacks		**Adequate**/~~not adequate,~~ **Efficacious**/~~not efficacious~~	

This certificate is valid for the audit report/ Audit Period only. However, it is subject to automatic cancellation in case of any change in product profile/capacity, quality and quantity of effluent emission (Air + Waste Water + Solid/Hazardous) and efficiency of EMS equipment.

This Certificate forms part of environmental audit report.

Name & Address of the Environmental Auditor

Environmental Engineering Laboratory, M. S. Patel Department of Civil Engineering,

Charotar University of Science & Technology,
CHARUSAT Campus, Changa, Dist.: Anand, State: Gujarat - 388 421

Signature of Environmental Auditor

Sr. No.	Name & Designation	Sign
1	**Mr. Gaurav V. Kapse** (Environmental Engineer)	
2	**Mr. Gaurav R. Patel** (Chemical Engineer)	
3	**Dr. Seema Amin** (Microbiologist)	
4	**Mr. Jinit R. Patel** (Chemist)	

Date: 9/7/2021

Place: Changa, Anand

Adequacy Certificate of Environmental Management System

The Environmental Engineering Laboratory, M. S. Patel Department of Civil Engineering, **Charotar University of Science & Technology**, **Changa** is recognized by the GPCB, Gandhinagar under the Environmental Audit Scheme introduced by the Hon'ble High Court Gujarat, vide its orders dated 20/12/1996 and 13/3/1997 and modified order dated 16/9/1999, as an environmental auditor for the purpose of the auditing, having carried out

Environmental audit of,

- M/s. Bodal Chemical Ltd. (Unit-VII)

- Located at: Plot NO.804, vill: DADHWADA,
Tal: Padra, Dist: Vadodara-394116
- Manufacturing products as under:

Sr. No.	Product Name	GPCB Production Limit as per CCA MT/Month
1	H-acid	150MT/Month
2	Beta Napthol	500 MT/Month
3	Acetanilide	650 MT/Month
4	Acetanilide ChloroSulphonated mass	500 MT/Month
5	Vinyl Sulphone (ACS Based)	300 MT/Month
6	Reactive red, Yellow and other	500 MT/Month
7	Reactive Black dyes(Ramazol dyes)	1250 MT/Month
8	Direct acid dyes	1250 MT/Month
9	Cogeneration Power Plant	5 MW
Total		**5200 MT/Month**
BY Product		
1	Glauber salt(from VS plant)	130 MT/Month
2	Glauber salt(from H-acid plant)	150 MT/Month
3	Acetic Acid	51 MT/Month
4	Gypsum Sludge	850 MT/Month

Having completed the environmental audit based on personal monitoring, and audit report, prepared as per the direction of the Hon'ble High Court in Environmental Audit Scheme, it is certified that the Environmental Management System (EMS) provided by this industry for the products manufactured and capacity as stated above is Adequate & Efficient to achieve the quality of effluents (Air + Wastewater + Solid Waste) as specified in consent/Notifications by GPCB, Gandhinagar for the following quantity of waste generation:

Liquid Effluent	Including Chemical Units	1. Industrial Effluent	452 KL/Day
		2. Domestic Wastewater (Sewage)	25 KL/Day
Solid Waste Solid Waste		1. Incineration Ash	As per the Consent
		2. Distillation Residues	
		3. Used Oil	
		4. Contaminated Discarded Containers/ Liners	
		5. Process sludge from filtration & neutralization	
		6. Iron sludge	
		7. Spent Sulphuric acid	
		8. HCL 30%	
Air Emissions Flue gas Stacks as well as process stacks		**Adequate**/~~not adequate,~~ **Efficacious**/~~not efficacious~~	

This certificate is valid for the audit report/ Audit Period only. However, it is subject to automatic cancellation in case of any change in product profile/capacity, quality and quantity of effluent emission (Air + Waste Water + Solid/Hazardous) and efficiency of EMS equipment.

This Certificate forms part of environmental audit report.

Name & Address of the Environmental Auditor

Environmental Engineering Laboratory, M. S. Patel Department of Civil Engineering,
Charotar University of Science & Technology,
CHARUSAT Campus, Changa, Dist.: Anand, State: Gujarat - 388 421

Signature of Environmental Auditor

Sr. No.	Name & Designation	Sign
1	**Dr. Dipeshkumar Sonaviya** (Environmental Engineer)	
2	**Mr. Gaurav R. Patel** (Chemical Engineer)	
3	**Dr. Seema Amin** (Microbiologist)	
4	**Mr. Jinit R. Patel** (Chemist)	

Date: 24/6/22

Place: Changa, Anand

True Copy

ANNEXURE R4-28

Atul Industries
Mfg. of Process Control & Electronics Instruments,Service Provider,Project Materials Suppliers
53, Karishma Society, Nr. Gayatri Mandir / Bus Depot, At. Po. & Ta. Padra
Dist. Vadodara - 391440 State - Gujarat, India. Ph No. +919429952126
E-mail: atulindustries83@yahoo.com
ISO 9001:2015

AI/BCLU7/23082206

Date: 23-08-2022

TO WHOMSOEVER IT MAY CONCERN

I am Chartered Engineer with Registration No. M 150264-0 Date 02.04.2015. My domain competence is in Mechanical.

This is to certify that M/s Bodal Chemicals Limited Unit 7 Dudhwada ECP Canal Road Ta : Padra, Dist : Vadodara with their technical details etc, with regard to their technical description / specification against each item & having due regard to relevant norms of process & recorded data of July 2022 of GROUND WATER REMEDIATIONPLANT. After technical scrutiny of relevant process designs & drawings with their recorded data.

We observed following details.

1. Installation date: JANUARY 2019
2. Capacity: 850m3 /day
3. Verification of data:
    a. Data Available from plant installation Month July 2022
    b. Relevant Process Norms

From recorded data analysis & performance testing of plant I found arbitrarily approximately 95% plant capacity.

Atul Soni Digitally signed by Atul Soni

Mr. A. K. SONI
CHARTERED ENGINEER

Atul Industries
Mfg. of Process Control & Electronics Instruments,Service Provider,Project Materials Suppliers
53, Karishma Society, Nr. Gayatri Mandir / Bus Depot. At. Po. & Ta. Padra
Dist. Vadodara - 391440 State - Gujarat. India. Ph No. +919429952126
E-mail: atulindustries83@yahoo.com
ISO 9001:2015

AI/BCLU7/23082204

Date: 23-08-2022

TO WHOMSOEVER IT MAY CONCERN

I am Chartered Engineer with Registration No. M 150264-0 Date 02.04.2015. My domain competence is in Mechanical.

This is to certify that M/s Bodal Chemicals Limited Unit 7 Dudhwada ECP Canal Road Ta : Padra, Dist : Vadodara with their technical details etc, with regard to their technical description / specification against each item & having due regard to relevant norms of process & recorded data of July 2022 of H-MEE (MEE-1, MEE-2,MEE-3) PLANT. After technical scrutiny of relevant process designs & drawings with their recorded data.

We observed following details.

1. Installation date: MAY 2014
2. Capacity: 185.700kL/day
3. Verification of data:
    a. Data Available from plant installation Month July 2022
    b. Relevant Process Norms

From recorded data analysis & performance testing of plant I found arbitrarily approximately 78% plant capacity.

Atul Soni Digitally signed by Atul Soni

Mr. A. K. SONI
CHARTERED ENGINEER

Atul Industries
Mfg. of Process Control & Electronics Instruments,Service Provider,Project Materials Suppliers
53, Karishma Society, Nr. Gayatri Mandir / Bus Depot, At. Po. & Ta. Padra
Dist. Vadodara - 391440 State - Gujarat, India. Ph No. +919429952126
E-mail: atulindustries83@yahoo.com
9001:2015

AI/BCLU7/23082205

Date: 23-08-2022

TO WHOMSOEVER IT MAY CONCERN

I am Chartered Engineer with Registration No. M 150264-0 Date 02.04.2015. My domain competence is in Mechanical.

This is to certify that M/s Bodal Chemicals Limited Unit 7 Dudhwada ECP Canal Road Ta : Padra, Dist : Vadodara with their technical details etc, with regard to their technical description / specification against each item & having due regard to relevant norms of process & recorded data of July 2022 of VS MEE PLANT (MEE-1, MEE-2). After technical scrutiny of relevant process designs & drawings with their recorded data.

We observed following details.

1. Installation date: MAY 2014
2. Capacity: 209kL/day
3. Verification of data:
    a. Data Available from plant installation Month July 2022
    b. Relevant Process Norms

From recorded data analysis & performance testing of plant I found arbitrarily approximately 79% plant capacity.

Atul Soni Digitally signed by Atul Soni

Mr. A. K. SONI
CHARTERED ENGINEER

Atul Industries
Mfg. of Process Control & Electronics Instruments, Service Provider, Project Materials Suppliers
53, Karishma Society, Nr. Gayatri Mandir / Bus Depot, At. Po. & Ta. Padra
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ISO 9001:2015

AI/BCLU7/23082203

Date: 23-08-2022

TO WHOMSOEVER IT MAY CONCERN

I am Chartered Engineer with Registration No. M 150264-0 Date 02.04.2015. My domain competence is in Mechanical.

This is to certify that M/s Bodal Chemicals Limited Unit 7 Dudhwada ECP Canal Road Ta : Padra, Dist : Vadodara with their technical details etc, with regard to their technical description / specification against each item & having due regard to relevant norms of process & recorded data of July 2022 of MEE S D PLANT 1&2. After technical scrutiny of relevant process designs & drawings with their recorded data.

We observed following details.

1. Installation date: OCTOBER 2016
2. Capacity: 33kL/day each plant
3. Verification of data:
    a. Data Available from plant installation Month July 2022
    b. Relevant Process Norms

From recorded data analysis & performance testing of plant I found arbitrarily approximately 90% plant capacity.

Atul Soni Digitally signed by Atul Soni

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This is to certify that M/s Bodal Chemicals Limited Unit 7 Dudhwada ECP Canal Road Ta : Padra, Dist : Vadodara with their technical details etc, with regard to their technical description / specification against each item & having due regard to relevant norms of process & recorded data of July 2022 of ETP MEE PLANT. After technical scrutiny of relevant process designs & drawings with their recorded data.

We observed following details.

1. Installation date: April 2018
2. Capacity: 125kL/day
3. Verification of data:
    a. Data Available from plant installation Month July 2022
    b. Relevant Process Norms

From recorded data analysis & performance testing of plant I found arbitrarily approximately 90% plant capacity.

Atul Soni
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Mr. A. K. SONI
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ISO 9001:2015

AI/BCLU7/23082202

Date: 23-08-2022

TO WHOMSOEVER IT MAY CONCERN

I am Chartered Engineer with Registration No. M 150264-0 Date 02.04.2015. My domain competence is in Mechanical.

This is to certify that M/s Bodal Chemicals Limited Unit 7 Dudhwada ECP Canal Road Ta : Padra, Dist : Vadodara with their technical details etc, with regard to their technical description / specification against each item & having due regard to relevant norms of process & recorded data of July 2022 of ETP ADVENT PLANT. After technical scrutiny of relevant process designs & drawings with their recorded data.

We observed following details.

1. Installation date: April 2018
2. Capacity: 320kL/day
3. Verification of data:
    a. Data Available from plant installation Month July 2022
    b. Relevant Process Norms

From recorded data analysis & performance testing of plant I found arbitrarily approximately 94% plant capacity.

Atul Soni Digitally signed by Atul Soni

Mr. A. K. SONI
CHARTERED ENGINEER

True Copy

ANNEXURE R4-29

THE FINAL REPORT
FOR
BODAL CHEMICALS LTD. (UNIT VII)

PROJECT TITLE:
ASSESSMENT OF THE ENVIRONMENTAL PERFORMANCE OF THE SEVEN INDUSTRIES UTILIZING THE COMMON CHANNEL OF VECL FOR CONVEYING THEIR TREATED WASTEWATERS AND ADVICE FOR IMPROVING THEIR RESPECTIVE PERFORMANCES

Submitted to:

Vadodara Enviro Channel Ltd.
Plot No. 304/1,317 & 318
At & Post: Dhanora,
Dist. Vadodara -391 346
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Submitted by

Prof. Shyam R. Asolekar
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23rd August, 2020

DECLARATION

This ***Final Report*** is prepared for submission to **M/s Vadodara Enviro Channel Limited, Vadodara** under the commitments made by IIT Bombay to VECL in connection with the ongoing project entitled *"Assessment of the Environmental Performances of the Seven Industries Utilizing the Common Channel of VECL for Conveying Their Treated Wastewaters and Advice for Improving Their Respective Performances"*. This project was officially started from 1st September, 2019.

This ***Final Report*** represents the work completed at **Bodal Chemicals Limited (hereafter referred to as "Bodal Unit VII")** by the undersigned during 1st September, 2019 and today.

All the data in the chapters on the industry under investigation were obtained from the respective industry. In addition, the undersigned declares that this *Report* represents his ideas – especially the interpretation of data, analysis of ETPs and any inferences drawn on the basis of the investigations. Wherever others' ideas or words have been included, the original sources have been adequately cited and referenced to. The undersigned also declares that he has adhered to the principles of academic honesty and integrity and has not misinterpreted or fabricated or falsified any idea/data/fact/source in his submission.

Shyam R.

Date:
23rd August, 2020

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REPORT ON

BODAL UNIT VII

1.1 Introduction

VECL intends to implement the identified modifications and achieve the ETP capability to process the effluents as per the stipulations prescribed by Gujrat Pollution Control Board (GPCB) in the said 7 non-compliant units. Accordingly, the project entitled "Assessment of the Environmental Performances of the Seven Industries Utilizing the Common Channel of VECL for Conveying Their Treated Wastewaters and Advice for Improving Their Respective Performances" has been envisioned. The FIVE (05) specific objectives of the proposed study have been articulated as follows:

1. To characterize and quantify waste streams including wastewaters, primary and secondary sludges, spent catalysts, spent clays, activated carbon, molecular sieves and zeolites, waste insulation materials, non-recyclable mixed contaminated solvents, waste oils and greases, end-of-life lead acid-batteries, filter-cartridges, membrane cartridges, used (to be discarded) packaging materials, containers, bags, etc. Also, collect the past-performance data of the said 7 ETPs. In addition, to collect the details of the production process and unit operations at the plant during the site visits – which are expected to take place immediately after commencement of the project (i.e. to conduct a kind of rapid and focused environmental audits of the 7 non-compliant units)

ACKNOWLEDGEMENTS: The author of this report and his team members would like to sincerely thank the following two groups of people:

(1) The management of Bodal Unit VII and all the concerned individuals for providing all the information instantaneously as well as answering several calls made by the team of IITB. We are humbled by their readiness and forthcoming co-operation. This investigation was impossible without their support!

(2) The personnel at VECL, especially Mr Satishbhai Panchal and his assistants, *namely*: Anurag Yadav and Riya Thakor. We have no words to thank them. We truly appreciate their frankness, decency and hard work. We cannot thank them enough!

2. Characterization and quantification of various waste-streams, sludges, skimmed oily emulsions and residues from the selected wastewater treatment equipment and unit operation in the respective ETP (from each of the 7 non-compliant units).
3. Suggest methods to improve the current waste disposal practice, as applicable, in the respective unit (for each of the 7 non-compliant units). This may include collection of additional samples, carrying out analysis, and any other required activities for establishing the advice.
4. After the assessment of all the wastes described above, effort shall be made to articulate modes of disposal alternative to the ones currently practiced by the 7 non-compliant units. This may include collection of samples, carrying out analysis, and any other required activities for establishing the mode of disposal.
5. Finally, the advice for improving the design and operation of the conveying channel will also be articulated for long life and uninterrupted operation of the 55 km long effluent channel.

Bodal Unit VII is a production unit working primarily in the area of production of dye intermediates (specifically H-Acid, ASC, Vinyl Sulphone, and β-Naphthol) and crude synthetic organic dyestuffs (specifically Remazol Black, Reactive Red and Yellow, and Acid Black Dyes). These dye intermediates are some of the most basic and important dye intermediates and have great demand in the dyestuff sector. These crude synthetic organic dyes are also of vital importance not only in India, but also internationally. The vital statistics related to production capacities, consumption of electrical energy, and description of utility facilities at Bodal Unit VII are presented in **Table 1.1**.

Bodal Unit VII typically manufactures about 1.7 thousand Tons of H-Acid per year, 3.5 thousand Tons of β-Naphthol per year, 1.7 thousand Tons of Acetanilide per year, 2.3 thousand Tons of Vinyl Sulphone per year, and 10 thousand Tons of Crude Dyes per year. In addition, the information regarding the various utilities in the plant is also given in the Table. Reportedly, Bodal Unit VII has a discharge permit of trade effluent of 452 m^3/day as authorized by GPCB (as per the "Consolidated Consent & Authorization" issued on 14 June, 2018) and by VECL for the purposes of discharge of treated wastewater into the Channel. It is also important to note that Bodal Unit VII has equipment for concentrating process effluents and for recovering water suitable for recycling in the process plants. Some process effluent is also let into the Effluent Treatment Plant (ETP) – which is eventually disposed of in the channel operated by VECL.

Table 1.1 The vital statistics related to production capacities, consumption of electrical energy, and description of utility facilities at Bodal Unit VII

Product / Energy	Quantity in 2018-19	Quantity in 2017-18	Batch or Continuous?
Product 1: H-Acid (Ton per year)	1,783.050	1,669.700	Batch
Product 2: β-Naphthol (Ton per year)	4,034.043	3,182.089	Batch
Product 3: Acetanilide (Ton per year)	1,750.550	1,727.900	Batch
Product 4: Vinyl Sulphone (Ton per year)	2,375.700	2,238.708	Batch
Product 5: Crude Dyes (Ton per year)	10,282.236	9,525.609	Batch
Electrical Energy Consumed (KWh per year)	16,263,268	27,110,707	Continuous

Utility Unit	Description & Capacity	Batch or Continuous?
Capacity of Steam Boiler (KLD)	IBR Steam Boiler-1: 192 KLD IBR Steam Boiler-2: 192 KLD IBR Steam Boiler-3: 360KLD IBR Steam Boiler for Dyes: 144 KLD	Batch
Capacity of Waste Heat Recovery Boilers of CPP (Ton per day)		
Capacity of Ice Plant (KLD)	118 KLD	Batch
Capacity of Cold-Water Utility (KLD)	1,400 KLD	Batch
Capacity of Hot-Water Utility (KLD)	Not Applicable	
Capacity of Cooling Tower (KLD)		
Capacity of Process Water Softening Plant (KLD)		
Capacity of Process Water R.O. Plant (KLD)	802 KLD	Batch
ETP Capacity (KLD)	474 KL per day	Batch
Crystallizer Capacity (TPD)		
MEE Capacity (KLD)	148 KL per day	Batch
Capacity of Spray Dryer (TPD)	13 Ton per Day	Batch

Permit for Discharging the trade effluent, as authorized by GPCB, in the “Consolidated Consent & Authorization” issued on 14 June, 2018	452 m^3/day

1.2 Brief Manufacturing Process of H-Acid

As stated earlier, Bodal Unit VII manufactures H-Acid and Vinyl Sulphone. The brief manufacturing process of H-Acid is presented in this section. The brief production process flow diagram of H-Acid is given in **Figure 1.1**. The major production process details are given below:

1. Sulphonation
    a. Charge Sulphuric Acid and Oleum (65%). Analyse the percentage acidity.
    b. Charge Naphthalene in the reactor. The reactor employed for this is a closed jacketed vessel.
    c. Charge the second batch of Sulphuric Acid and check acidity.
    d. Charge the second batch of Oleum to the reaction mass and check acidity. Gradually heat the reaction mass.
    e. Cool the reacting mass in the Chiller The complete Sulphonation step will take 48-60 hours to complete.
    f. Blow the reaction mass to Nitration vessel.
2. Nitration
    a. The sulphonated mass received from Sulphonation vessel is first cooled in a jacketed vessel.
    b. Charge Water into the reactor and check acidity. Then, cool the reaction mass to 55ºC.

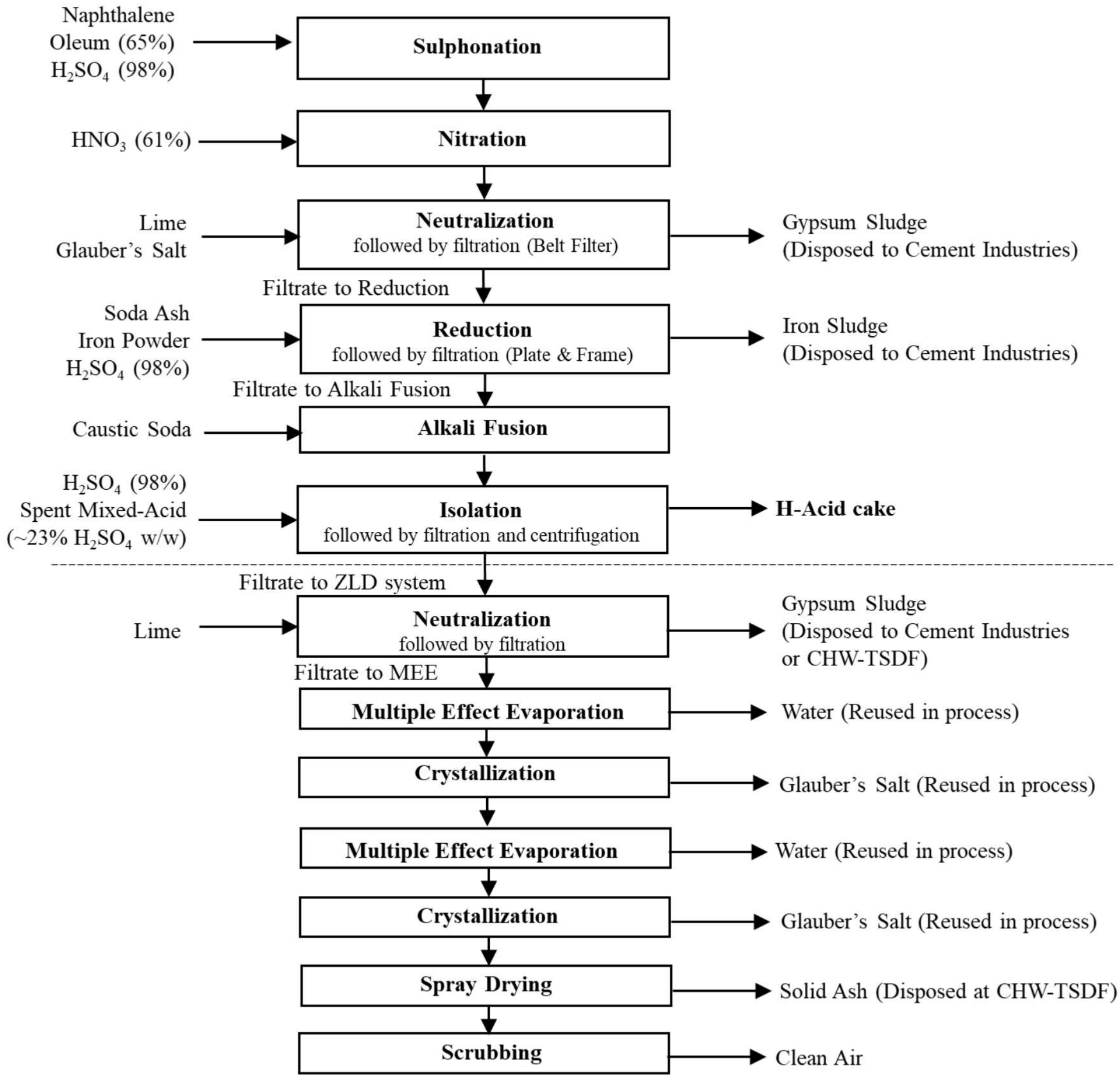


Figure 1.1 Production Process Flow Diagram of H-Acid at Bodal Unit VII

c. Charge first batch of 60% Nitric Acid gradually and the cool the reaction mass to 40ºC.

d. Charge the second batch of Nitric acid at 40ºC and check the acidity.

e. The reaction will lead to formation and emission of NOx.. The Nox gases are scrubbed in the Alkali scrubber to give Sodium Nitrite ($NaNO_2$) which is a by-product used in Dye manufacturing.

f. Transfer the reaction mass to Neutralization vessel.

3. Neutralization

a. Take freshwater and filtrate wash water (from the filtration of Gypsum Sludge after Neutralization step) from the previous batch.

b. This reaction takes place in a Mild Steel Rubber Lined (MSRL) reaction vessel.

c. Charge Glauber's Salt ($Na_2SO_4.7H_2O$) in the form of slurry into the Neutralization reactor.

d. Prepare Limestone slurry using recycled water. Charge the limestone slurry from limestone slurry vessel such that foaming is avoided. This process takes about 3 hours.

e. Emission of Nox also takes place during transfer of the nitro mass into the Neutralization vessel. This NOx is also taken to the Alkali Scrubber for obtaining Sodium Nitrite as the by-product.

f. Thus, Gypsum ($CaSO_4$) will be formed and precipitated.

g. Filter the reaction mass on Nutche filter to obtain Gypsum 'Sludge'. Give water washes to adjust filtrate (Nitro solution) volume as per requirement.

h. Separate the wash-water to be reused in the next batch for Lime Slurry preparation.

i. Transfer the filtrate to the Reduction vessel.

4. Reduction

   a. The neutralized mass is transferred from the previous stage.

   b. The reactor used in this reaction is Acid Proof-Brick lined vessel.

   c. Slowly add Sulphuric Acid such that *p*H is maintained between 5 to 5.5 and heat the reaction mass.

   d. Charge the first lot of CI powder (Fe^0) and the first lot of neutralized nitro solution.

   e. Charge second lot CI Powder.

   f. Stir the reaction mass while maintaining the temperature at about 95-100ºC. This reaction might take about 18-20 hours to complete.

   g. Check if Reduction is complete by taking the Nitrite Value (NV).

   h. If Reduction is complete, then charge Soda Ash (Na_2CO_3) and maintain the *p*H between 8 and 8.5.

   i. Filter the reduced Nitro solution (now Amino solution) in Filter Press to obtain ‘Iron Sludge’.

   j. Collect the wash water from the Filter Press in the holding tank for further press washing.

   k. Send the filtrate from the Filtration operation to the Evaporator for recovery of water.

   l. Receive the dilute Amino solution filtrate from Filter Press in the Evaporator.

   m. Evaporate and concentrate the dilute Amino solution to a concentration of 35-40% w/w Amino solution. Check sample NV.

5. Fusion

    a. Receive the concentrated Amino solution from the Evaporator and charge Caustic flakes (solid NaOH flakes) while stirring.

    b. Remove the Water until the reaction mass becomes a paste. Then, check the Alkalinity of the paste.

    c. Charge Methanol under pressure. Gradually heat up the reaction mass to 178ºC in 3 to 3.5 hours. The temperature and pressure are maintained at 178-180ºC and 24-26 kg/cm^2 respectively, then cool the reaction mass.

    d. Distil and condense the Methanol for reuse in the next batch.

6. Isolation

    a. Receive the Spent Mixed-Acid from Vinyl Sulphone into the Isolation vessel.

    b. Add the fused amino mass in the reactor.

    c. Due to the reaction, SO_2 gas will be generated which is subjected to scrubbing in the Alkali Scrubber to obtain Sodium Sulphite ($NaHSO_3$) as a by-product.

    d. The H-Acid is precipitated.

    e. Subject the reaction mass with the H-Acid product to Nutche filtration and Centrifugation. The precipitated H-Acid forms the filter cake.

    f. Check the amount of loss of product in Filtrate (often known as 'Mother Liquor'). It is generally about 3.5 to 4% w/w of the Filtrate from Nutche filter and Centrifuge. The Filtrate is sent to the Zero Liquid Discharge (ZLD) system for recovery of water as well as recovery of Glauber's Salt.

    g. Finally, dry the cake in Flash Dryer to obtain H-Acid final product cake.

    h. Pack in HDPE bags.

7. The Zero Liquid Discharge (ZLD) System

A brief description of the unit operations in the ZLD system is given below:

a. Neutralization: The excess Sulphuric Acid from the Isolation step is neutralized with Lime to form Gypsum Sludge. The Filtrate is then sent to the Crystallizer for recovery of Glauber's Salt.

b. Concentration: The 'Mother Liquor' is then passed through first Triple-Effect Evaporator (MEE) concentrator to evaporate the water part of the 'Mother Liquor'. This recovered water (known as 'Condensate') is condensed and reused in the process, as well as in other parts of the plant. The 'Concentrate' from MEE step is sent to the first Crystallizer.

c. Crystallization: The concentrated 'Mother Liquor' is then sent to the first Crystallizer for separating out the Glauber's Salt. The Glauber's Salt is separated continuously by employing a Pusher Centrifuge. After separation, the 'Mother Liquor' is sent to Multiple Effect Evaporator for recovery of water.

d. Concentration: The 'Mother Liquor' is then passed through second Triple-Effect Evaporator (MEE) concentrator to evaporate the water part of the 'Mother Liquor'. This recovered water (known as 'Condensate') is condensed and reused in the process, as well as in other parts of the plant. The 'Concentrate' from MEE step is sent to the second Crystallizer.

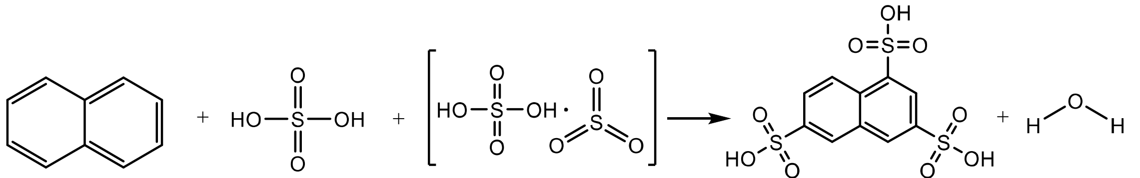
e. Crystallization: The concentrated 'Mother Liquor' is then sent to the first Crystallizer for separating out the Glauber's Salt. The Glauber's Salt is separated continuously by employing a Pusher Centrifuge. After separation, the 'Mother Liquor' is sent to Spray Dryer for final removal of water.

f. Spray Dryer: Finally, the 'Concentrate' from the MEE is subjected to Spray Drying to obtain 'ash', which is then temporarily stored on-site then packed and disposed of in CHW-TSDF.

1.3 Stoichiometry and Mass Balance for H-Acid Production

As discussed earlier, Section 1.2 illustrates the production process flow diagram for H-Acid, as practised in the batch-wise production, at Bodal Unit VII. At the outset, all the important reactions performed in the production process of H-Acid are briefly presented below:

1. Sulphonation



Naphthalene
Chemical Formula: $C_{10}H_8$
Molecular Weight: 128.17

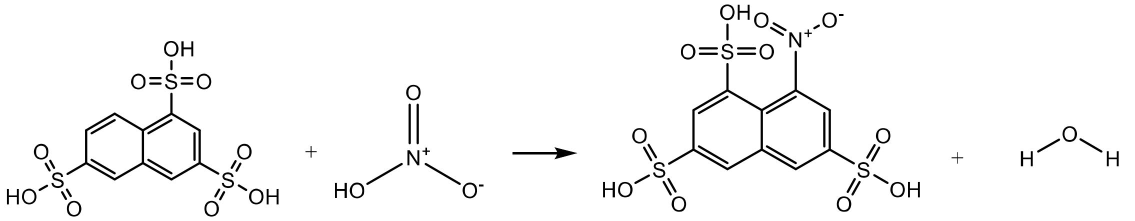
Sulphuric Acid
Chemical Formula: H_2O_4S
Molecular Weight: 98.07

Oleum (65%)
Chemical Formula: $H_2O_4S.O_3S$
Molecular Weight: 178

Naphthalene-1,3,6-trisulphonic acid
Chemical Formula: $C_{10}H_8O_9S_3$
Molecular Weight: 368.35

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

2. Nitration



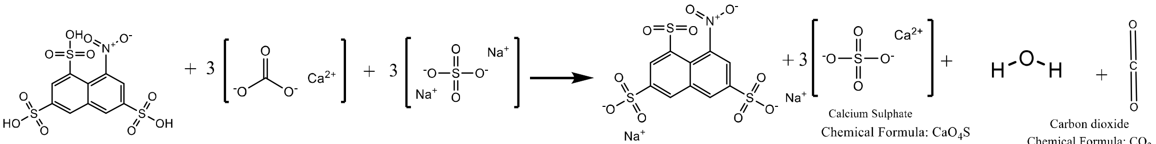
Naphthalene-1,3,6-trisulphonic acid
Chemical Formula: $C_{10}H_8O_9S_3$
Molecular Weight: 368.35

Nitric Acid
Chemical Formula: HNO_3
Molecular Weight: 63.01

1-Nitronaphthalene-3,6,8-trisulphonic acid
Chemical Formula: $C_{10}H_7NO_{11}S_3$
Molecular Weight: 413.34

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

3. Neutralization



1-Nitronaphthalene-3,6,8-trisulphonic acid
Chemical Formula: $C_{10}H_7NO_{11}S_3$
Molecular Weight: 413.34

Calcium Carbonate
Chemical Formula: $CCaO_3$
Molecular Weight: 100.09

Sodium Sulphate
Chemical Formula: Na_2O_4S
Molecular Weight: 142.04

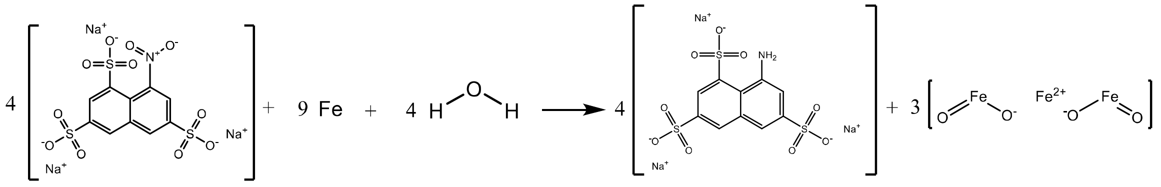
1-Nitronaphthalene-3,6,8-trisulphonate sodium salt
Chemical Formula: $C_{10}H_4NNa_3O_{11}S_3$
Molecular Weight: 479.29

Calcium Sulphate
Chemical Formula: CaO_4S
Molecular Weight: 136.13

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

Carbon dioxide
Chemical Formula: CO_2
Molecular Weight: 44.01

4. Reduction



1-Nitronaphthalene-3,6,8-trisulphonate sodium salt
Chemical Formula: $C_{10}H_4NNa_3O_{11}S_3$
Molecular Weight: 479.29

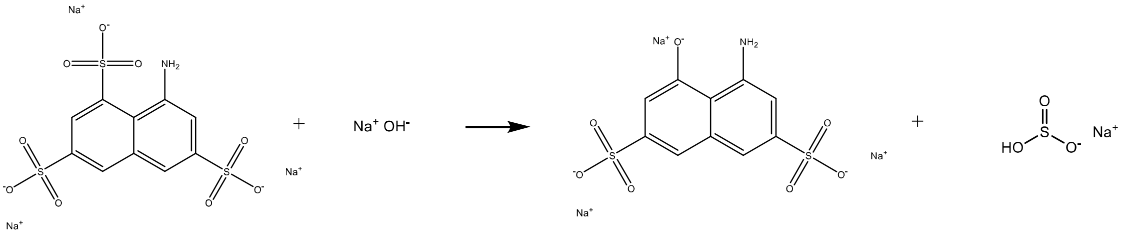
Iron
Chemical Formula: Fe
Molecular Weight: 55.85

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

1-Aminonaphthalene-3,6,8-trisulphonate sodium salt
(Koch Acid or T-Acid Trisodium Salt)
Chemical Formula: $C_{10}H_6NNa_3O_9S_3$
Molecular Weight: 449.31

Iron (II, III) Oxide (Magnetite)
Chemical Formula: Fe_3O_4
Molecular Weight: 232

5. Caustic Fusion



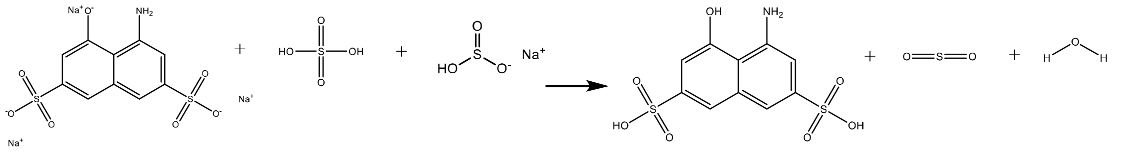
1-Aminonaphthalene-3,6,8-trisulphonate sodium salt
(Koch Acid or T-Acid Trisodium Salt)
Chemical Formula: $C_{10}H_6NNa_3O_9S_3$
Molecular Weight: 449.31

Caustic Soda
Chemical Formula: NaOH
Molecular Weight: 40

Sodium-4-amino-5-oxidonaphthalene-2,7-disulfonate
(H-Acid Trisodium Salt)
Chemical Formula: $C_{10}H_6NNa_3O_7S_2$
Molecular Weight: 385.25

Sodium Bisulphite
Chemical Formula: $HNaO_3S$
Molecular Weight: 104.05

6. Isolation



Sodium-4-amino-5-oxidonaphthalene-2,7-disulfonate
(H-Acid Trisodium Salt)
Chemical Formula: $C_{10}H_6NNa_3O_7S_2$
Molecular Weight: 385.25

Sulphuric Acid
Chemical Formula: H_2O_4S
Molecular Weight: 98.07

Sodium Bisulphite
Chemical Formula: $HNaO_3S$
Molecular Weight: 104.05

1-Amino-8-naphthol-3,6-disulfonic acid
(H-Acid)
Chemical Formula: $C_{10}H_9NO_7S_2$
Molecular Weight: 319.30

Sulphur Dioxide
Chemical Formula: O_2S
Molecular Weight: 64.06

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant “as a production unit” is presented in **Figure 1.2**; with the basis of 1 Ton production of H-Acid at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of H-Acid synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

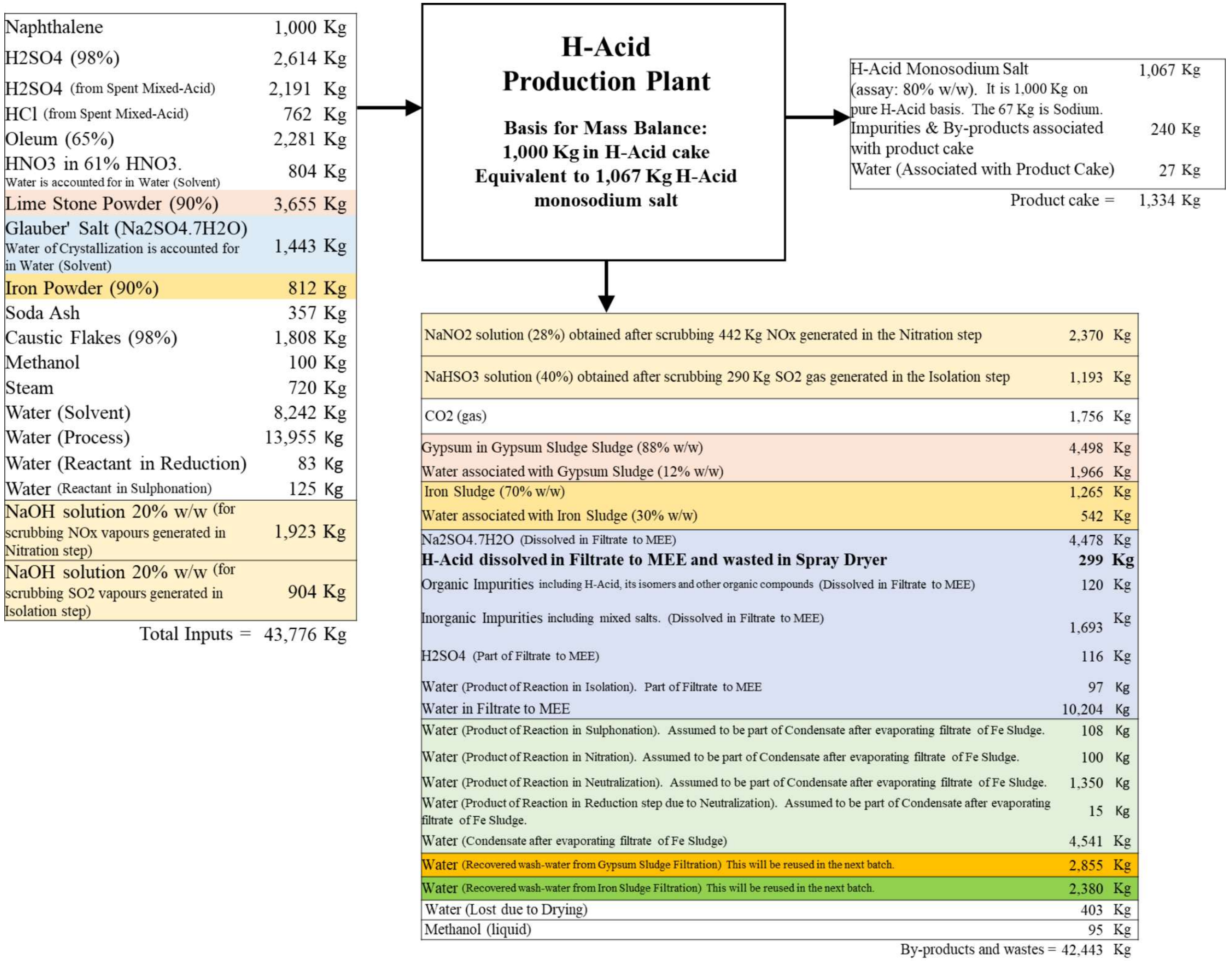
It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing H-Acid molecule is elaborated in this analysis. **Table 1.2** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of H-Acid at Bodal Unit VII. As presented in the Table, 1 Ton of H-Acid production also produces 1.461 Ton of Water (as a by-product). This water, however, remains mixed with the bulk of the reacting mass in the reactor and eventually gets removed downstream through one or more unit operations.

Further, **Table 1.3** depicts the detailed 'Water Budget' for production of one Ton of H-Acid at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the H-Acid production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 24.586 Ton per Ton of H-Acid production. More importantly, Table 1.3 also elaborates on all the efforts of reuse and recycle of the recovered water within the process plant. Because of these efforts, a substantial quantity of water is being saved and reused (19.426 Ton of water per Ton of H-Acid production). This is the high point in process innovation – because of which nearly 79% water is being recycled.

In summary, the net freshwater requirement works out to be 5.16 Ton of water per Ton of H-Acid production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of moisture associated with product cake, solid waste disposed of in CHW-TSDF or sent to cement industries as well as on account of evaporation losses (see Table 1.3).

In summary, the net freshwater requirement works out to be 5.16 Ton of water per Ton of H-Acid production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of moisture associated with product cake, solid waste disposed of in CHW-TSDF or sent to cement industries as well as on account of evaporation losses (see Table 1.3).

It is the considered opinion of the author of this Report that the so-called "Filter Loss" comprising of 299 Kg of H-Acid per Ton production of H-Acid (refer to Figure 1.2) is neither believable nor economically and environmentally sustainable. This reported loss of product is apparently sent to the landfill in CHW-TSDF. If this is the fact, the production process of H-Acid employed by Bodal Unit VII is indeed a primitive and unacceptable process and provides enough ground for considering banning it. Such extremely polluting and wasteful process must not be practiced!



Naphthalene	1,000 Kg
H2SO4 (98%)	2,614 Kg
H2SO4 (from Spent Mixed-Acid)	2,191 Kg
HCl (from Spent Mixed-Acid)	762 Kg
Oleum (65%)	2,281 Kg
HNO3 in 61% HNO3. Water is accounted for in Water (Solvent)	804 Kg
Lime Stone Powder (90%)	3,655 Kg
Glauber' Salt (Na2SO4.7H2O) Water of Crystallization is accounted for in Water (Solvent)	1,443 Kg
Iron Powder (90%)	812 Kg
Soda Ash	357 Kg
Caustic Flakes (98%)	1,808 Kg
Methanol	100 Kg
Steam	720 Kg
Water (Solvent)	8,242 Kg
Water (Process)	13,955 Kg
Water (Reactant in Reduction)	83 Kg
Water (Reactant in Sulphonation)	125 Kg
NaOH solution 20% w/w (for scrubbing NOx vapours generated in Nitration step)	1,923 Kg
NaOH solution 20% w/w (for scrubbing SO2 vapours generated in Isolation step)	904 Kg
Total Inputs =	43,776 Kg

H-Acid Production Plant

Basis for Mass Balance:
1,000 Kg in H-Acid cake
Equivalent to 1,067 Kg H-Acid monosodium salt

H-Acid Monosodium Salt (assay: 80% w/w). It is 1,000 Kg on pure H-Acid basis. The 67 Kg is Sodium.	1,067 Kg
Impurities & By-products associated with product cake	240 Kg
Water (Associated with Product Cake)	27 Kg
Product cake =	1,334 Kg

NaNO2 solution (28%) obtained after scrubbing 442 Kg NOx generated in the Nitration step	2,370 Kg
NaHSO3 solution (40%) obtained after scrubbing 290 Kg SO2 gas generated in the Isolation step	1,193 Kg
CO2 (gas)	1,756 Kg
Gypsum in Gypsum Sludge Sludge (88% w/w)	4,498 Kg
Water associated with Gypsum Sludge (12% w/w)	1,966 Kg
Iron Sludge (70% w/w)	1,265 Kg
Water associated with Iron Sludge (30% w/w)	542 Kg
Na2SO4.7H2O (Dissolved in Filtrate to MEE)	4,478 Kg
H-Acid dissolved in Filtrate to MEE and wasted in Spray Dryer	**299 Kg**
Organic Impurities including H-Acid, its isomers and other organic compounds (Dissolved in Filtrate to MEE)	120 Kg
Inorganic Impurities including mixed salts. (Dissolved in Filtrate to MEE)	1,693 Kg
H2SO4 (Part of Filtrate to MEE)	116 Kg
Water (Product of Reaction in Isolation). Part of Filtrate to MEE	97 Kg
Water in Filtrate to MEE	10,204 Kg
Water (Product of Reaction in Sulphonation). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	108 Kg
Water (Product of Reaction in Nitration). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	100 Kg
Water (Product of Reaction in Neutralization). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	1,350 Kg
Water (Product of Reaction in Reduction step due to Neutralization). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	15 Kg
Water (Condensate after evaporating filtrate of Fe Sludge)	4,541 Kg
Water (Recovered wash-water from Gypsum Sludge Filtration) This will be reused in the next batch.	2,855 Kg
Water (Recovered wash-water from Iron Sludge Filtration) This will be reused in the next batch.	2,380 Kg
Water (Lost due to Drying)	403 Kg
Methanol (liquid)	95 Kg
By-products and wastes =	42,443 Kg

Figure 1.2 Input-output analysis of H-acid at Bodal Unit VII (Basis: 1,000 Kg of H-Acid & 1,400 Kg of H-Acid monosodium salt in product cake)

Table 1.2 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of H-Acid at Bodal Unit VII

Role of Water in the Process Plant	**Quantity per Ton of H-Acid production (Kg)**
Water (as one of the Reactants in Sulphonation)	125
Water (as one of the Reactants in Reduction)	83
Water (Product of Reaction in Isolation). Part of Filtrate to MEE	-97
Water (Product of Reaction in Sulphonation). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	-108
Water (Product of Reaction in Nitration). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	-100
Water (Product of Reaction in Neutralization). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	-1,350
Water (Product of Reaction in Neutralization of acid in Reduction step). Assumed to be part of Condensate after evaporating filtrate of Fe Sludge.	-15
Net Water Consumption (in reactive steps) =	**-1,461 ***

* 1,461 Kg of water is generated during production of one Ton of H-Acid.

Table 1.3 A detailed ‘Water Budget’ for production of one Ton of H-Acid at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the H-Acid production plant.

Role of Water in the Process Plant	**Quantity per Ton of H-Acid production (Kg)**
Input of Water (Basis: 1 Ton of H-Acid)	
Water (added as Solvent)	8,450
Water (generated in reactive steps from the past batch)	1,461
Water (consumed in several unit operations)	13,955
Water (consumed in generation of Steam)	720
Total input of water for one Ton of H-Acid =	**24,586**
Emission of Water (Basis: 1 Ton of H-Acid)	
Water associated with damp Gypsum Sludge (12% w/w) to cement industry	-1,966
Recovered washing water from filtration of Gypsum Sludge	-2,855
Washing water reused and recycled in the next batch	2,855
Water associated with damp Iron Sludge (30% w/w) to cement industry	-542
Recovered washing water from filtration of Iron Sludge	-2,380
Washing water reused and recycled in the next batch	2,380
Water associated with Gypsum Sludge (settling of the last Filtration step after Isolation step; separated in ZLD section). Sent to CHW-TSDF or cement industry.	-434
Water recovered as Condensate from MEE (total mother liquor = 10,458 Kg) [434+4,105+3,973+1,788 = 10,300]	-4,105
Reused and recycled Condensate water from MEE	-4,105
Water of crystallization (Glauber’s salt, $Na_2SO_4.7H_2O$) output of Crystallizer	-3,973
Indirect water recycling due to reuse of Glauber’s salt in the process	3,973
Water lost in evaporation from Spray Dryer (which is operated at 500ºC)	-1,788
Water (Condensate from single-stage Concentrator employed for evaporation of filtrate after separation of Fe Sludge, using P/F filter)	-6,113
Reused and recycled water Condensate from single-stage Concentrator	6,113
Water (lost in drying the H-Acid cake)	-403
Water (Associated with Product Cake)	-27
Total emission of water for one Ton of H-Acid =	**-24,586**
Condensate Water reused from various sources	**19,426**
Water leaving the system (associated with solids & evaporation loss)	**-5,160**
Net freshwater requirement (24,586 – 19,426 = 5,160)	**5,160**

1.4 Gap Analysis for H-Acid Production

Gap refers to the space between "where we are" (the present state) and "where we want to be" (the target state). A gap analysis may also be referred to as a needs analysis, needs assessment or ***Need-Gap Analysis***.

The first step in conducting the so-called *Need-Gap Analysis* is to establish the specific target objectives by looking at the company's immediate and long term interest (mission statement, strategic goals and improvement objectives). The next step is to analyze current business processes by collecting relevant data on performance levels and how resources are presently allocated to these processes. This data can be collected from a variety of sources depending on what is being analysed. For example, by looking at documentation, conducting interviews with the experts and production managers, brainstorming and observing the production process. Lastly, after comparing the company's current state against the desirable and mandatory environmental as well as work-place safety requirements; a comprehensive plan can be developed. Such "plan" outlines the specific steps to take to fill the gap between its current and future states, and reach its target objectives.

Small and medium scale industries, in particular, can benefit from performing such *Need-Gap Analysis*. <u>Such analysis could have the following THREE target objectives</u>:

1. How to allocate resources?,
2. How to improve performance and profits? and
3. How to improve work-place safety and minimize environmental pollution loads?

In the following section, an effort has been made to present the improvements for <u>short-term benefits</u> as well as <u>long-term benefits</u>; based on the methodology described above.

<u>Improvements for Short-Term Benefits</u>

Significance of Temperature Control: Although the literature on the production process and efficiency improvement is limited, several Chinese patents (and a limited number of patents from other countries) are apparently available. However, owing to the issues associated with language barrier and cryptic details typically reported in patent documents, this literature did not prove to be useful in suggesting measures for improving the production process and efficiency of H-Acid production. In any case, we understand that there are several different steps, unit processes, and unit operations involved in the production of H-Acid. Some of these processes need to be operated over a very slim temperature range because the raw materials and intermediates involved in the unit process are temperature sensitive.

It is well understood that the kinetics of the steps involved in H-Acid production are rather complex and therefore, "manual control" of temperature proves to be inferior when compared with the so-called "automatic control". Inadequate temperature control causes the formation of unwanted isomers and side products – which eventually lead to wastage of raw materials or intermediates and, thus, lead to enhanced generation of wastewater and undesirable by-products. Needless to emphasise here that the overall yield of the desirable product, too, diminishes significantly in absence of sophisticated temperature control instrumentation – which further leads to a decrease in profits.

In view of the above kinetics-related issues, installation of the automatic temperature control instrumentation as well as sophisticated temperature measurement instrumentation are strongly recommended. Devising two separate instruments, one for automatic temperature control and one sophisticated temperature measurement is considered the best-practise for industrial chemical production. The redundancy and duplication in control and measurement instrumentation often proves to be a wise investment in the long run. Not only it improves the product yield and profits, but it also improves the process safety and decreases pollution.

Automation of Acid and / or Alkali Addition: By using a digital *p*H meter and linking it to the addition of acid / alkali in each unit process, stoichiometric addition of acid and / or alkali would be relatively easy. Thus, excessive addition of acid and / or alkali would be minimised and ultimately the quantity of salts dissolved in the reacting mass would decrease. These dissolved salts are carried forward to the treatment and recovery plant and finally end up in the mixed solid residue which is disposed of in CHW-TSDF. Through the closer control of *p*H in the respective reactors, especially in the isolation step, the H-Acid loss in the concentrated streams could also be minimised to a considerable extent.

Reportedly, there are about 50 isomeric compounds present in the reacting mass of H-Acid. These other compounds are hindrances and effectively reduce the yield of H-Acid production. Apparently, the industry standard for the yield of H-Acid is only about 50-55% of the theoretical value. There could be the following three reasons for the formation of unwanted isomers; while synthesizing H-Acid:

a. Inherent limitations in the kinetics of various reaction stages which ultimately lead to the formation of isomers,

b. Improper control of reaction parameters like temperature, pressure, *etc.*, and

c. Excessive usage of acids and alkalis starting from sulphonation to isolation step. Due to this, sodium salts (NaCl and Na_2SO_4) get accumulated in the H-Acid slurry, further inhibiting the precipitation rate of H-Acid in the acidic medium.

In addition to the formation of unwanted isomers, the filtrate separated by Nutche Filter as well as the mother liquor separated through Centrifugation after the Isolation step is known to carry the soluble H-Acid and the other isomers (commensurate with the thermodynamic equilibrium) with it. This is generally termed as 'Filter loss' and it is reportedly about 300-400 Kg per Ton of H-Acid production. This soluble 'Filter loss' is comprised of mixed Naphthalene based compounds including H-Acid, Koch Acid, and other compounds.

In view of the above thermodynamic and kinetics-related issues, installation of the sophisticated digital *p*H control instrumentation as well as automated systems for acid / alkali addition are strongly recommended. Devising two separate systems, one for sophisticated *p*H control and one for automated addition is considered the best-practise for industrial chemical production. The redundancy and duplication in these systems often proves to be a wise investment in the long run. Not only it improves the product yield and profits, but it also improves the process safety and decreases pollution.

Significance of Digital Flowmeters to Track Water Usage: As seen in the water budget, production of H-Acid and VS is highly water-intensive. Keeping a track of water at every input and the output is essential from the point of view of having an accurate water balance and water budget. Currently, since there is no flow meter to keep track of the water usage, the values of the water usage are rough estimates. This is unacceptable. In order to have a perfect mass balance and water balance, every part of the water used in the plant needs to be tracked.

<u>Therefore, the use of digital flowmeters at all the places in the plant where water is used is recommended</u>. The planning and implementation of this recommendation should be expedited and taken up as the first priority.

Significance of Acetic Acid in Reduction Process: The Reduction step in H-Acid production process is related to conversion of nitro group to amine group in the aromatic ring of nitronapthalene trisulfonic acid. Conventionally, this is achieved by implementing the so-called "Bechamp Reduction Process". This reduction process consists of the following steps:

(1) addition of acid to generate H^+ ions,

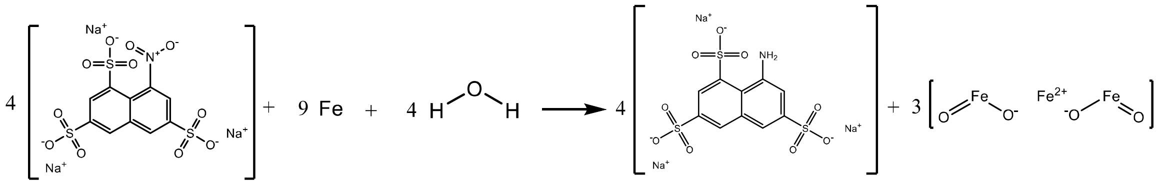
(2) addition of iron powder,

(3) adsorption of the nitronapthalene trisulfonic acid on to the iron particles,

(4) the reduction reaction taking place on the iron particles, and

(5) desorption from the iron to give the reduced aminonapthalane trisulfuric acid and iron oxide (Fe_3O_4 or Magnetite).

Overall Reaction:



1-Nitronaphthalene-3,6,8-trisulphonate sodium salt
Chemical Formula: $C_{10}H_4NNa_3O_{11}S_3$
Molecular Weight: 479.29

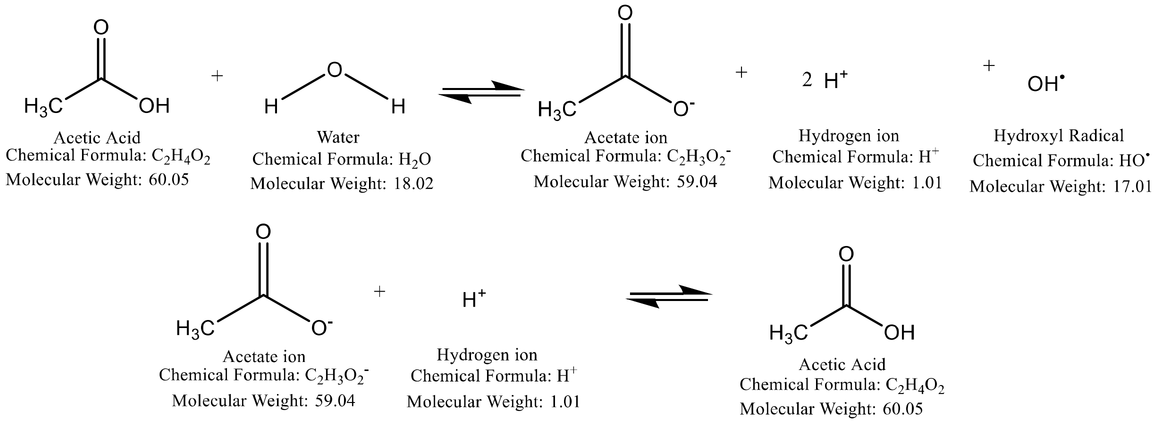
Iron
Chemical Formula: Fe
Molecular Weight: 55.85

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

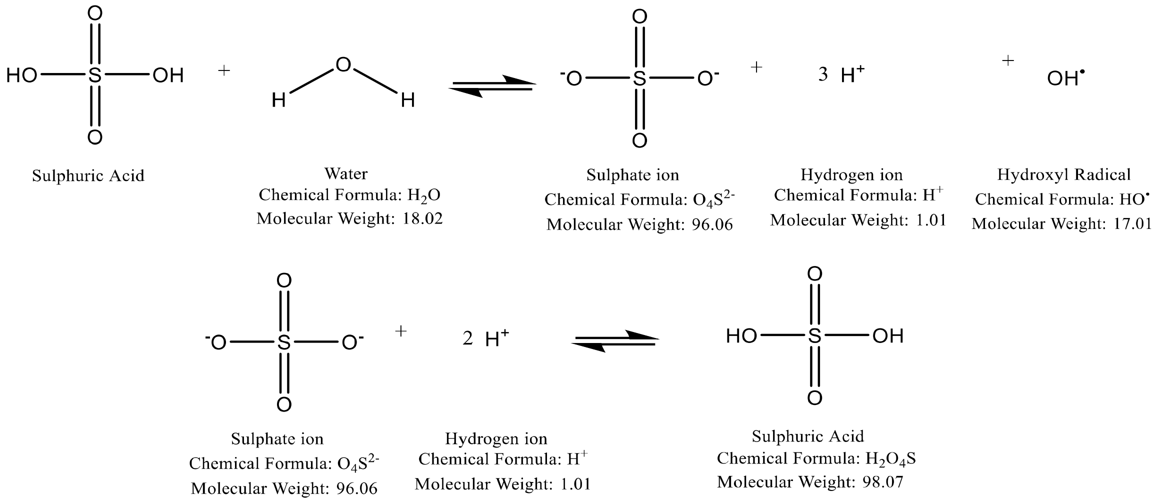
1-Aminonaphthalene-3,6,8-trisulphonate sodium salt
Chemical Formula: $C_{10}H_6NNa_3O_9S_3$
Molecular Weight: 449.31

Iron (II, III) Oxide (Magnetite)
Chemical Formula: Fe_3O_4
Molecular Weight: 232

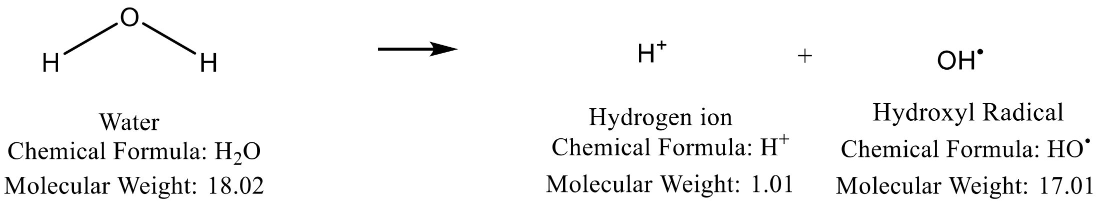
This can be achieved using two different acids, *namely*: Sulphuric Acid or Acetic Acid. It is interesting to note that, in Bechamp process, the acid used in the Reduction process does not react with the nitro-compound directly. It merely facilitates maintenance of adequate concentration of H^+ ions in the reacting mass. For example, if one uses Acetic Acid, the following two reactions will take place wherein the Acetic Acid would dissociate and again get constructed as per the following reactions and generate net "one excess H+ ion" per molecule of Acetic Acid.



Alternately, H_2SO_4 can also be used and analogously generate net “one excess H+ ion” per molecule of H_2SO_4:



Thus, the same following overall reaction could be constructed in the events of using Sulphuric Acid or Acetic Acid and therefore it may appear as though Sulphuric Acid may be the alternate for Acetic Acid in the Reduction process.



As reported in the literature on ‘Bechamp Reduction’ process, use of mineral acid, as well as organic acid, is possible. But, typically, a disclaimer is also announced regarding the use of mineral acids: The Reduction process is *p*H sensitive and the recommended range for operation for *p*H of the reacting mass is 5.5 to 6.9. Clearly, only a small quantity of acid is sufficient since the previous stage is Neutralization, and the reaction mass is slightly alkaline. Furthermore, the possibility always exists that mineral acids might encourage side reactions and / or formation of undesirable products. Keeping this in mind, it is generally recommended to use a weak acid, such as Acetic Acid, instead of a strong mineral acid such as Sulphuric Acid. It appears that the selectivity of reduction of nitro group is debatable (and thus its potential for improving the overall yield of H-Acid) in the event of use of Acetic Acid. Thus, it is imperative to carry out careful and well-monitored R&D for Reduction process in H-Acid synthesis in laboratory using, both, Acetic Acid and Sulphuric Acid.

When Sulphuric Acid is used in the Reduction process, the elemental Iron is oxidized to form Ferrous Sulphate ($FeSO_4$). Ferrous Sulphate has a markedly high solubility in water (25.6 g $FeSO_4$ /100 mL Water) and thus, will more or less remain in the filtrate and not be associated with the 'Iron Sludge' cake. This dissolved $FeSO_4$ contributes to the overall TDS and imparts a bluish colour to the reaction liquid. The same does not happen with Acetic Acid because Ferrous Acetate is not a stable compound, and the Acetic Acid will remain in the filtrate. Clearly, the dissolved $FeSO_4$ load in the filtrate is minimized by using Acetic Acid. Thus, the use of Acetic Acid will lead to a comparatively higher yield of the 'Iron Sludge' in the Filtration after the Reduction step. Use of Acetic Acid instead of Sulphuric Acid seems to have multiple tangible advantages. The only downside to using an organic acid this is that Acetic Acid ultimately ends up in the Mother Liquor and thereby increases COD (typically, 85.6 Kg per ton of H-Acid production). In any case, since Acetic Acid is highly bio-degradable, it may not be a great cause for concern.

In summary, the targeted short-term R&D will need to be conducted to assess the relative benefits of using Acetic Acid over Sulphuric Acid in the Reduction process and switch to Acetic Acid. Thus, the techno-economically defendable decision can be made. This issue is important because it has, both, environmental and commercial implications.

Recycling Excess Sulphuric Acid from Nitration Step in Isolation of H-Acid: It is well known that the Sulphonation and Nitration reactions must be conducted in extremely acidic conditions involving excess Sulphuric Acid. Hence, in the Nitration step, after completion of the reaction, Nitronaphthalene trisulphonic acid is obtained along with excess unreacted Sulphuric Acid. The gaseous NOx is drawn off from the reactor.

Thus, we now have a Nitronaphthalene trisulphonic acid and Sulphuric Acid mixture. As reported in a patent and other literature, this mixture (from current batch) can be taken to the final Isolation stage (of a previous batch) in which Sulphuric Acid is a reactant. Thus, formation and precipitation of H-Acid takes place using the Nitro-Sulphuric Acid mixture obtained after Nitration. The H-Acid is precipitated and filtered off. The filtrate thus obtained is sent directly to the Reduction step. In this way, a cyclic process utilizing all streams and minimizing waste streams is obtained. In fact, it is reported in a certain patent that this process has a comparatively higher yield of H-Acid.

This process has the following advantages:

1. Complete usage of excess acids.
2. Elimination of the Neutralization and Filtration steps after Nitration. Thus, eliminating the Gypsum Sludge waste stream.
3. Reduction of usage of excess bases for neutralization, thus leading to a reduction in the TDS.
4. By reducing the usage of Spent Mixed-Acid from ASC, a reduction in the COD of the filtrate after Isolation will take place – COD of Spent Mixed-Acid is estimated to be around 80,000 mg/L.

The targeted R&D, therefore, will need to be taken up with high priority to evaluate how the process of recycling of acidic effluent from Nitration step to Isolation step (and filtrate used in the Reduction step) can be applied to the prevailing H-Acid production process. The benefits of this alternate process are numerous and the ultimate reduction of the environmental load bolsters the case for its applicability. Along with this, the costs of purchasing the patent must be taken into consideration if any.

Housekeeping and Maintenance: The investigation team from IIT Bombay visited this plant several times and discussed with persons from Production and Environment Protection teams. There was a great cooperation from these persons and the information was furnished efficiently through emails, completing the requested tabulated information, cooperating with the personnel from Vadodara Enviro Channel Limited (VECL) while collecting samples and obtaining data as well as through face-to-face interactions during the site visits. The IIT Bombay team is grateful to the company for the help and facilitation.

Frankly, whenever IIT Bombay team visited the production facility as well as ETP and STP, *prima facie* it appeared as though the overall upkeep and housekeeping was visibly poor. Most of the floors and surfaces inside the roof and columns of the shed were unclean, rusted and it was clear that the housekeeping related functions were generally given a low priority.

It is generally understood that the functions related to routine maintenance of equipment, reactors, piping, loading-unloading platforms, and staircases (ladders) become difficult and the overall surroundings have poor housekeeping. It is also understood that the frequency of maintenance, too, increases in the midst of unclean surroundings (more corrosion, frequent breakdown, difficulty in repairs and maintenance).

More importantly, the propensity for accidents, fire, explosion, injury at the workplace are generally found to enhance in the situations where overall maintenance and housekeeping is poor. The modern safety science, in fact, has been lately recommending for superlative interventions related to cleanliness, daily upkeep, and above all, the "preventive maintenance".

Maintenance and calibration of all instrumentation and control hardware is of utmost importance, not only from the point of view of the production process and product purity but also from the point of view of minimization of pollution and enhancement of health and safety of the workers. Poorly or rarely calibrated instrumentation and control hardware will often lead to addition of an incorrect amount of inputs to the reactor or give a false picture of the conditions in the reactor. This might, in turn, impact the indoor air quality, safety of the workers, and generation of pollution from the production plant. If the production plant is not properly maintained, the probability of malfunctioning of the instrumentation and process control devices would increase. Also, the functioning of ETP and STP will get affected beyond the certain extent of negligence in the production plant.

In sum, it is well-known that the H-Acid production process is extremely complicated and rather highly polluting. No wonder, several states in India and several countries in the world have imposed a ban on the production of these dye-intermediates. Because the raw materials and intermediates involved in the production of H-Acid are extremely reactive and corrosive; the maintenance routine should be commensurate with the propensity of rusting and evolution of fumes in the process plant.

Clearly, poor maintenance and upkeep could generate an unsafe work environment and pose higher risk to the workers' safety and environment. In addition to this, safety devices such as relief valves, process control equipment, pressure relief valves, etc. must be maintained and replaced as per the industry standards and the best-recommended practices.

The investigation team from IIT Bombay has taken a serious note of these facts and would recommend rather strongly that the housekeeping and maintenance should be improved remarkably in the nearest future. Adequate Personal Protective Equipment (PPE), uniform for all personnel, labelling of equipment, tanks and pipelines should be taken up as the first priority and serious efforts should be made to create the positive first impression.

Constructing a New and Robust Stormwater Collection and Treatment System: The investigation team from IIT Bombay visited Bodal Unit VII multiple times and has taken note of the fact that the stormwater collection system is inadequate in its current installation. Bodal Unit VII produces H-Acid and Vinyl Sulphone. It is a well-known fact that although the H-Acid final product is a greyish-white powder, H-Acid solutions in water have a dark blue to blackish colour even at low concentrations. This property of H-Acid is the primary reason that the stormwater runoff from the H-Acid plant and its surrounding areas will more often than not have a dark blue or blackish colour and some amount of COD.

A new stormwater drainage system should be constructed which will adequately intercept the surface water and stormwater runoff as per industry standards and divert the water to the ETP for treatment. Since the stormwater from this industry will have COD contributed by highly recalcitrant organic compounds, under no condition should the surface water runoff and/or stormwater runoff be let off into the channel or the environment without treatment in the ETP first. Hence, a new and robust stormwater collection and treatment system must be constructed to intercept and treat the stormwater and surface water runoff as per industry standards. This endeavour must be taken up as the first priority.

Construction of Dedicated Shed for Temporary Storage of Fly Ash and Sludge Before Disposal: The investigation team from IIT Bombay has noticed that the storage areas of fly ash, Gypsum Sludge, and Iron Sludge in Bodal Unit VII need to be renovated. The current 'storage yards' are distributed at many places on the campus of the industry and it might be useful to renovate aimed at modernization of all storage areas.

The storage area of fly ash and sludges must be covered and must have a concrete base surrounded by a leak-proof dike to collect the oozing water and any leachate. The dike should be devised with pumping facility to transfer the liquid collected in the dike to ETP for further treatment before disposal in the VECL channel. This effort must be taken up as the first priority.

Improvements for Long-Term Benefits

Following are the suggestions for interventions that could potentially yield the so-called "long-term benefits":

Upgradation of Sulphonation Step: The Sulphonation step makes use of excess Sulphuric Acid in order to drive the reaction to completion and minimise the formation of by-products. This excess acid thus needs to be neutralized in the following steps. Hence, it is of utmost importance to upgrade and optimize the Sulphonation step. The following measures can be implemented to improve the yield of the sulphonation step:

a. Carrying out sulfonation using falling film or thin-film reactor is believed to be better from the perspectives of kinetics and mass transfer.

b. Currently, the entire mass in the sulphonation reactor is carried to the next reactor and then neutralized. Instead, separating sulphuric acid from the reaction mass, concentrating it, and eventually reusing it would be beneficial from environmental and economic perspectives.

Thus, the targeted R&D, thus, will need to be conducted in order to conclusively determine whether the application of a Thin Film Reactor will prove to be beneficial to the H-Acid production process. The R&D of the proposed 'separation, concentration, and reuse of the excess Sulphuric Acid' must be taken up to determine the various technological options and their applicability. Comprehensive laboratory experiments need to be conducted and the scientific evidence should be used to make a decision.

Efforts to Explore Methods for Elimination of Gypsum Sludge: The Sulphonation step makes use of excess Sulphuric Acid in order to drive the reaction to completion and minimise the formation of by-products. This excess acid thus needs to be neutralized. In order to separate the nitro naphthalene sulphonic acid from sulphuric acid, the mass is reacted with lime. This results in conversion of sulphuric acid to Calcium Sulphate

($CaSO_4$) – which results in approximately 8 tonnes of gypsum sludge per Ton of H-acid production. Further, this wet gypsum sludge reportedly contains 0.5 to 1% w/w nitro naphthalene compounds.

It is reported that through solvent extraction of organic acid from the inorganic acid, followed by distillation system, pure nitro naphthalene sulphonic acid could be produced and the gypsum sludge generation could be eliminated. Since losses of desired product in Gypsum Sludge will decrease, adoption of this technology, will in fact, have a positive impact the purity of the H-acid produced.

However, targeted R&D and a detailed techno-economic feasibility study has to be conducted to ascertain the application of the Solvent Extraction and Distillation technology.

Efforts to Explore Methods for Elimination of Iron Sludge: The Reduction step in H-Acid production process is related to the conversion of nitro group to amine group in the aromatic ring of nitronapthalene trisulfonic acid. Conventionally, this is achieved by implementing the so-called "Bechamp Reduction Process". This Reduction process results in the generation of approximately 1.5 to 2 Ton of iron sludge per tonne of H-acid. Reportedly, the concentration of aminonaphthalene sulphonic acids in iron sludge was analysed to be about 4-5% w/w. The aminonaphthalene sulphonic acids are toxic and carcinogenic in nature.

By employing a 'Catalytic Reduction' process using gaseous hydrogen on the active surface of a metallic catalyst, it is possible to eliminate iron sludge generation as well as increase the yield of the Reduction reaction.

In summary, using a Catalytic Reduction process will have the following benefits:

(1) Yield can be improved by using Hydrogen gas for reduction.

(2) Elimination of the iron sludge formation.

(3) The other functional groups are not touched hence the formation of by-production is minimized.

(4) This will also avoid the need for the present lime neutralization step preceding the Reduction step.

Although the Catalytic Reduction process has a superior performance, it also comes with higher associated costs. It is well-known that the Bechamp Reduction process is suitable for smaller production scales and the Catalytic Reduction process is best suitable for larger scales of production.

However, targeted R&D efforts are required in this direction in order to arrive at a cost-effective catalytic reduction system catering to the scale of operation prevailing in this industry. These efforts will not only increase the present yield and quality of H-acid production but also eliminate the pollution problem due to high chloride and sulphate contaminate wastewater streams generated from these reaction steps.

1.5 Brief Manufacturing Process of Vinyl Sulphone

The brief manufacturing process, the stoichiometry and gap analysis of H-Acid production plant were presented in sections 1.2 through 1.4. The brief manufacturing process of Vinyl Sulphone is presented in this section. At Bodal Unit VII, the Vinyl Sulphone production process is split in two parts. The first one being the production of Acetyl Sulphonyl Chloride (ASC) and the second one being Vinyl Sulphone with ASC as its raw material. The ASC product manufactured here is also sent to other units of Bodal Dyes and Chemicals which use ASC as a raw material in their production processes.

Brief Manufacturing Process of ASC:

The brief production process flow diagram of ASC is given in **Figure 1.3**. The major production process details are given below:

1. Sulphonation
    a. Chlorosulphonic acid is taken into a MS jacked vessel and gradual addition of Acetanilide is carried out.
    b. The gases generated during Cholrosulphonation (namely HCl and SO_2) are taken to Air Pollution Control system for scrubbing.

c. The mixture of HCl and SO_2 gases are first subjected to water scrubbing (in the first two stages of a three-stage scrubbing system) to obtain dilute HCl solution as a by-product.

d. In the third stage, alkali scrubbing is performed with dilute NaOH solution to obtain Sodium Bisulphite solution as a by-product.

2. Dumping / Drowning

   a. Water is added to the reaction mass for decomposition of the excess unreacted Chlorosulphonic Acid.

   b. The reaction mixture is then drowned in an Ice-Water mixture in order to arrest the reaction. The water used here is actually the wash water filtrate from the previous batch. This also increases the ‘flowability’ of the reaction mixture.

   c. The decomposition reaction leads to release of SO_2 and HCl gases which are again subjected to the same scheme of three-stage scrubbing.

   d. The cold temperature leads to the precipitation of the ASC mass.

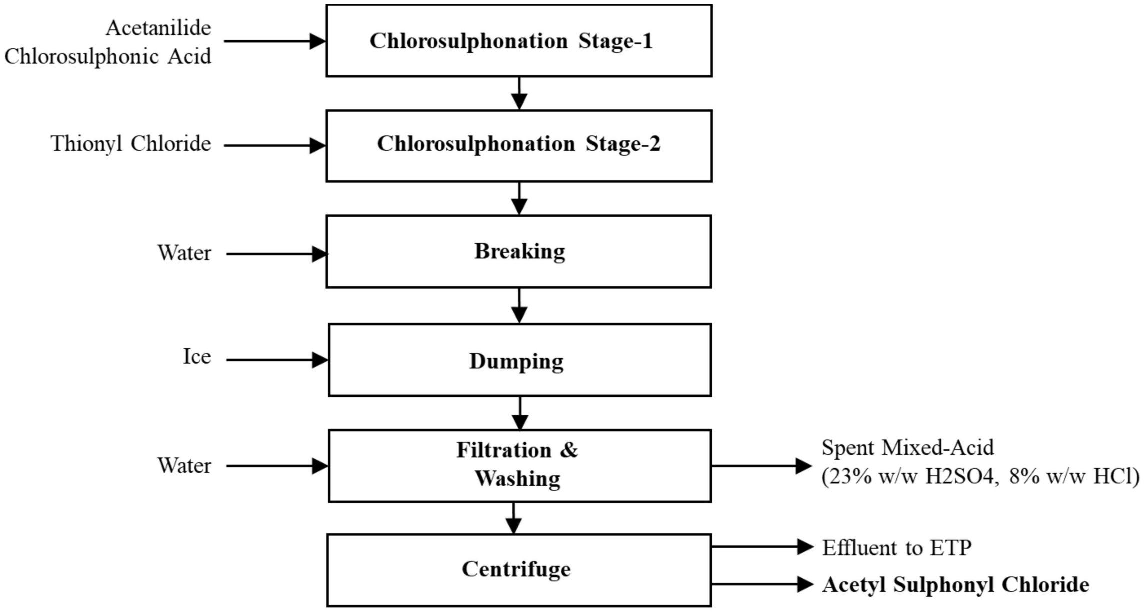


Figure 1.3 The production process flow diagram for ASC, as practised in the batch-wise production, at Bodal Unit VII

3. Filtration and Washing
    a. The reaction mass is subjected to filtration in a Nutche filter to separate the ASC cake from the reaction mass.
    b. The filtrate thus obtained is the Spent Mixed-Acid containing approx. 23% w/w H2SO4 and 8% w/w HCl along with 2% w/w several dissolved organics and 66% w/w water.
    c. The filter cake is washed and the filtrate of the washing water is reused in subsequent batches.
4. Centrifuge
    a. The ASC cake is centrifuged in order to remove the excess moisture.
    b. Thus, the ASC powder cake is obtained and packed.

Brief Manufacturing Process of Vinyl Sulphone:

The brief production process flow diagram of Vinyl Sulphone is given in **Figure 1.4**. The major production process details are given below:

1. Reduction
    a. Sodium Bisulphite and Caustic Lye slurry is prepared and ASC is slowly added to this mass for reduction.
    b. The *p*H is maintained at 7 by addition of Sulphuric Acid. The reduction slurry is then heated up to 55ºC.
    c. The "reduced mass" is then sent to the Condensation step.
2. Condensation / Ethoxylation
    a. Ethylene Oxide is passed in the "reduced mass" solution at neutral *p*H. The temperature is then maintained at 50ºC.
    b. The neutral pH is maintained by addition of the Spent Mixed-Acid generated in the Drowning step.

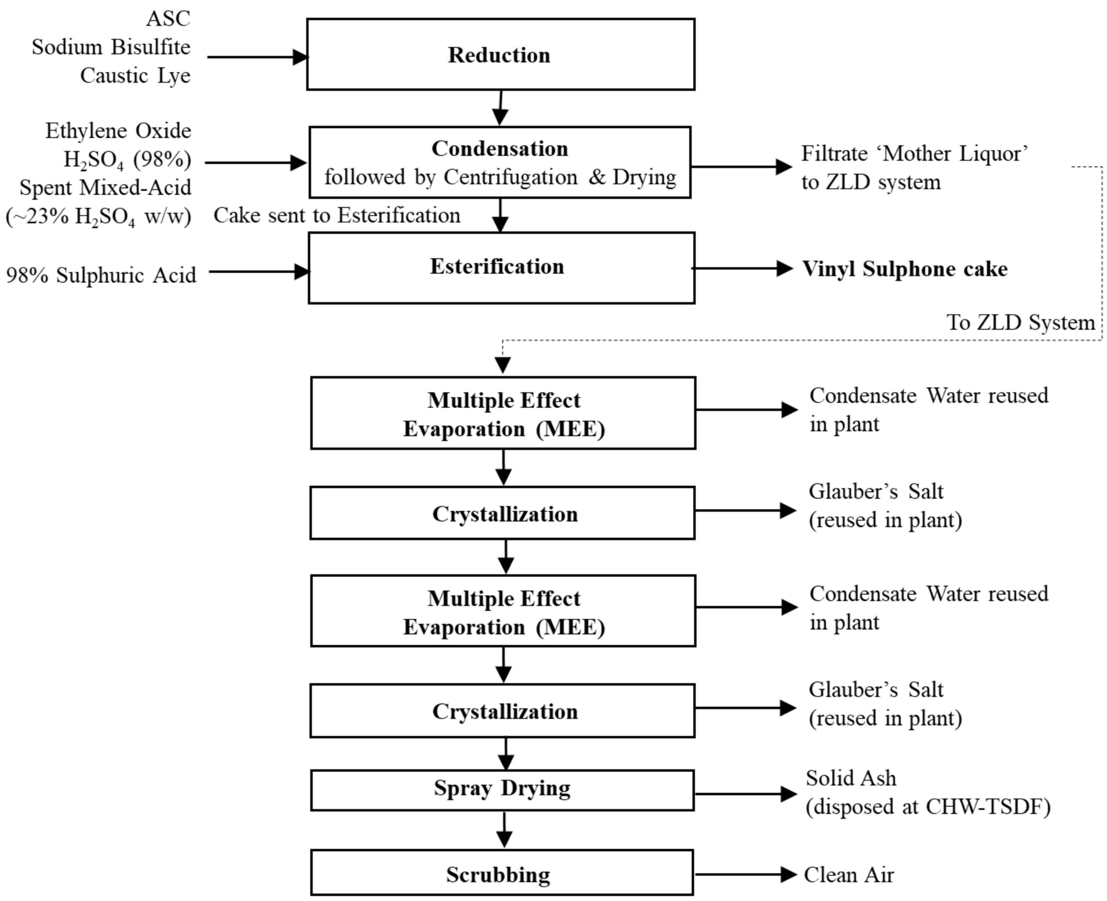


Figure 1.4 The production process flow diagram for Vinyl Sulphone, as practised in the batch-wise production, at Bodal Unit VII

c. The reaction product or slurry is allowed to cool and then filtered through Nutche Filter under vacuum. This is commonly referred to as the "condense mass".

d. The wet cake is washed with water followed by Centrifugation. The filtrate or 'Mother Liquor' has high organic and salt concentration which is sent to the ZLD system for concentration, recovery and disposal.

e. The retained solid mass is dried and sent to the final step.

3. Esterification

a. The dry "condense mass" is Esterified with Sulphuric Acid at the temperature of about 160ºC.

b. The 'Vinyl Sulphone Ester', or simply 'Vinyl Sulphone,' is formed after Esterification.

c. Acetic Acid is recovered as by product through Distillation during the Esterification reaction. The recovered Acetic Acid is reused in the manufacturing process of Acetanilide.

d. The solid material received after Esterification is pulverized, blended and packed in the bags.

4. The Zero Liquid Discharge (ZLD) System

A brief description of the unit operations in the ZLD system is given below:

a. Concentration: The 'Mother Liquor' is then passed through first Triple-Effect Evaporator (MEE) concentrator to evaporate the water part of the 'Mother Liquor'. This recovered water (known as 'Condensate') is condensed and reused in the process, as well as in other parts of the plant. The 'Concentrate' from MEE step is sent to the first Crystallizer.

b. Crystallization: The neutralized 'Mother Liquor' is then sent to the first Crystallizer for separating out the Glauber's Salt. The Glauber's Salt is separated continuously by employing a Pusher

Centrifuge. After separation, the 'Mother Liquor' is sent to Multiple Effect Evaporator for recovery of water.

c. Concentration: The 'Mother Liquor' is then passed through second Triple-Effect Evaporator (MEE) concentrator to evaporate the water part of the 'Mother Liquor'. This recovered water (known as 'Condensate') is condensed and reused in the process, as well as in other parts of the plant. The 'Concentrate' from MEE step is sent to the second Crystallizer.

d. Crystallization: The neutralized 'Mother Liquor' is then sent to the first Crystallizer for separating out the Glauber's Salt. The Glauber's Salt is separated continuously by employing a Pusher Centrifuge. After separation, the 'Mother Liquor' is sent to Spray Dryer for final removal of water.

e. Spray Dryer: Finally, the 'Concentrate' from the MEE is subjected to Spray Drying to obtain 'ash', which is then temporarily stored on-site then packed and disposed of in CHW-TSDF.

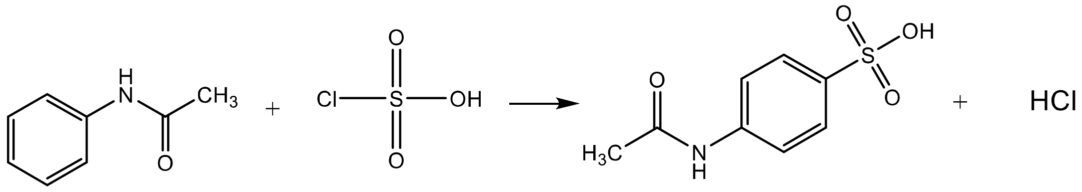
1.6 Stoichiometry and Mass Balance for Vinyl Sulphone Production

As discussed earlier, Figure 1.3 and Figure 1.4 illustrate the production process flow diagram for ASC and Vinyl Sulphone, as practised in the batch-wise production, at Bodal Unit VII. At the outset, all the important reactions performed in the production process of ASC and Vinyl Sulphone are briefly presented below:

Similar to the previous section, the stoichiometry and mass balance for Vinyl Sulphone production is split in two parts. The first one being for production of ASC and the second one being for the production of Vinyl Sulphone from ASC.

Stoichiometry and Mass Balance for ASC production:

1. Chlorosulphonation

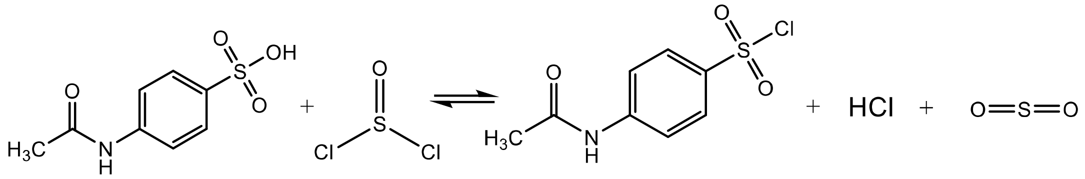


Acetanilide
Chemical Formula: C_8H_9NO
Molecular Weight: 134

Chlorosulphonic Acid
Chemical Formula: $ClHO_3S$
Molecular Weight: 117

4-Acetamidobenzenesulfonic Acid
Chemical Formula: $C_8H_9NO_4S$
Molecular Weight: 215

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36



4-Acetamidobenzenesulfonic acid
Chemical Formula: $C_8H_9NO_4S$
Molecular Weight: 215

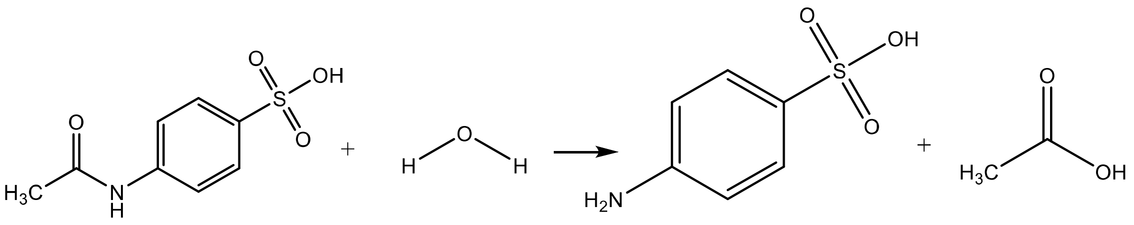
Thionyl Chloride
Chemical Formula: Cl_2OS
Molecular Weight: 119

4-Acetamidobenzenesulfonyl chloride
Chemical Formula: $C_8H_8ClNO_3S$
Molecular Weight: 234

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36

Sulphur Dioxide
Chemical Formula: O_2S
Molecular Weight: 64

2. Drowning

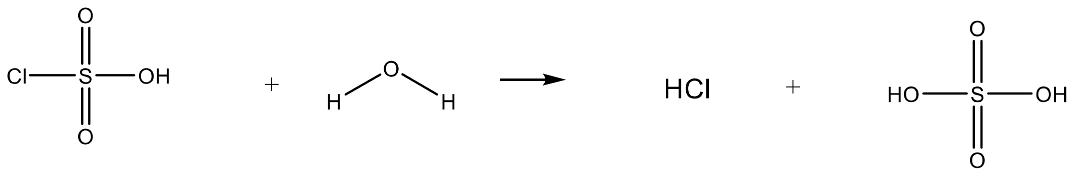


4-Acetamidobenzenesulfonic acid
Chemical Formula: $C_8H_9NO_4S$
Molecular Weight: 215

Water
Chemical Formula: H_2O
Molecular Weight: 18

Sulphanilic Acid
Chemical Formula: $C_6H_7NO_3S$
Molecular Weight: 173

Acetic acid
Chemical Formula: $C_2H_4O_2$
Molecular Weight: 60



Chlorosulphonic Acid
Chemical Formula: $ClHO_3S$
Molecular Weight: 117

Water
Chemical Formula: H_2O
Molecular Weight: 18

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36

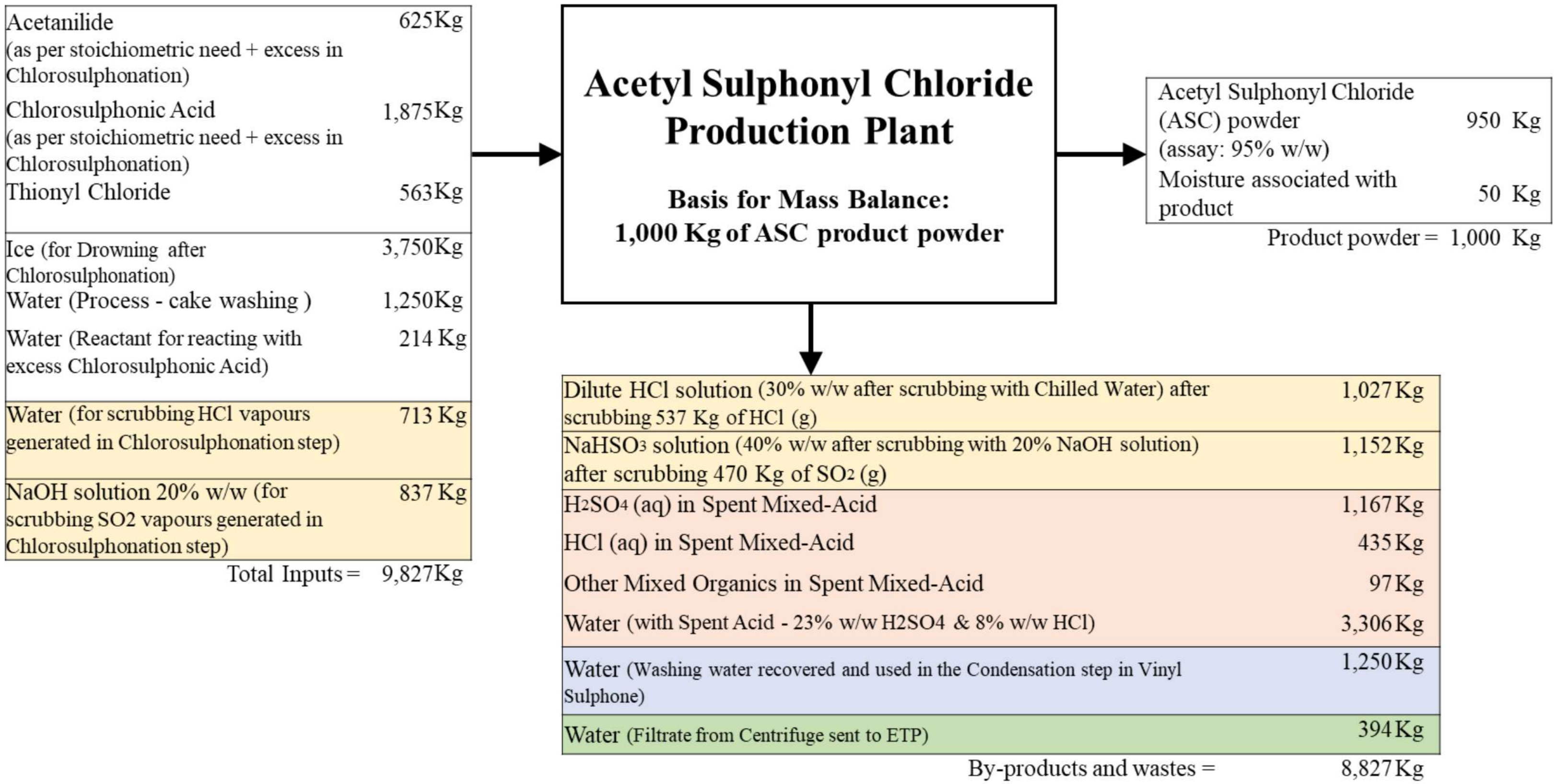
Sulphuric Acid
Chemical Formula: H_2O_4S
Molecular Weight: 98

With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant "as a production unit" is presented in **Figure 1.5**; with the basis of 1 Ton production of ASC at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of Vinyl Sulphone synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing ASC molecule is elaborated in this analysis. **Table 1.4** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of ASC at Bodal Unit VII. As presented in the Table, 1 Ton of ASC production also consumes 214 Kg of Water. This water, however, reacts and gets transformed.

Critical Discussion on the Water Budget: Further, **Table 1.7** depicts the detailed 'Water Budget' for production of one Ton of ASC at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the ASC and Vinyl Sulphone production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 5.214 Ton per Ton of ASC production. More importantly, Table 1.5 also elaborates on all the efforts of reuse and recycle of the recovered water within the process plant. Because of these efforts, a substantial quantity of water is being saved and reused (4.556 Ton of water per Ton of ASC production). This is the high point in process innovation – because of which nearly 87% water is being recycled.

In summary, the net freshwater requirement works out to be 0.658 Ton of water per Ton of ASC production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of moisture associated with product cake, solid waste disposed of in CHW-TSDF or sent to cement industries as well as on account of evaporation losses (see Table 1.7).



Acetanilide (as per stoichiometric need + excess in Chlorosulphonation)	625Kg
Chlorosulphonic Acid (as per stoichiometric need + excess in Chlorosulphonation)	1,875Kg
Thionyl Chloride	563Kg
Ice (for Drowning after Chlorosulphonation)	3,750Kg
Water (Process - cake washing)	1,250Kg
Water (Reactant for reacting with excess Chlorosulphonic Acid)	214 Kg
Water (for scrubbing HCl vapours generated in Chlorosulphonation step)	713 Kg
NaOH solution 20% w/w (for scrubbing SO2 vapours generated in Chlorosulphonation step)	837 Kg
Total Inputs =	9,827Kg

Acetyl Sulphonyl Chloride (ASC) powder (assay: 95% w/w)	950 Kg
Moisture associated with product	50 Kg
Product powder =	1,000 Kg

Dilute HCl solution (30% w/w after scrubbing with Chilled Water) after scrubbing 537 Kg of HCl (g)	1,027Kg
$NaHSO_3$ solution (40% w/w after scrubbing with 20% NaOH solution) after scrubbing 470 Kg of SO_2 (g)	1,152Kg
H_2SO_4 (aq) in Spent Mixed-Acid	1,167Kg
HCl (aq) in Spent Mixed-Acid	435Kg
Other Mixed Organics in Spent Mixed-Acid	97Kg
Water (with Spent Acid - 23% w/w H2SO4 & 8% w/w HCl)	3,306Kg
Water (Washing water recovered and used in the Condensation step in Vinyl Sulphone)	1,250Kg
Water (Filtrate from Centrifuge sent to ETP)	394Kg
By-products and wastes =	8,827Kg

Figure 1.5 Input-output analysis of Acetyl Sulphonyl Chloride (ASC) at Bodal Unit VII (Basis: 1,000 Kg of ASC product powder)

Table 1.4 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of ASC at Bodal Unit VII.

Role of Water in the Process Plant	**Quantity per Ton of ASC production (Kg)**
Water (as Reactant) for reacting with excess Chlorosulphonic Acid	214
Net Water Consumption (in reactive steps) =	**214 ***

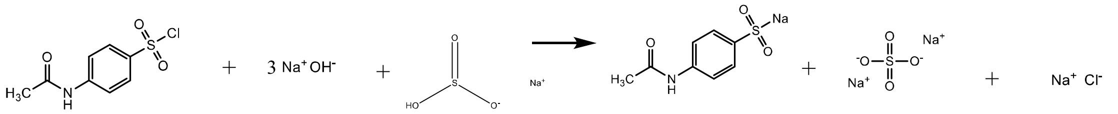
* 214 Kg of water is consumed during production of one Ton of ASC.

Table 1.5 A detailed 'Water Budget' for production of one Ton of ASC at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the H-Acid production plant.

Role of Water in the Process Plant	**Quantity per Ton of ASC production (Kg)**
Input of Water (Basis: 1 Ton of ASC)	
Water (Process - cake washing) This is taken from last batch	1,250
Ice (for Drowning after Chlorosulphonation)	3,964
Total input of water for one Ton of ASC =	**5,214**
Emission of Water (Basis: 1 Ton of ASC)	
Water emitted (in form of Filtrate after Drowning) (This will be used in the next batch.)	-1,250
Reused and recycled water (Filtrate after Drowning from previous batch)	1,250
Water (in Spent Mixed-Acid having 23% w/v H_2SO_4 & 8% w/v HCl)	-3,306
Reused and recycled water from Spent Mixed-Acid	3,306
Water sent to ETP	-608
Water associated with product cake	-50
Total input of water for one Ton of ASC =	**-5,214**
Condensate Water reused from various sources	**4,556**
Water leaving the system (associated with solids & evaporation loss)	**-658**
Net freshwater requirement (5,214 – 4,556 = 658)	**658**

Stoichiometry and Mass Balance for Vinyl Sulphone production:

1. Reduction



4-Acetamidobenzenesulfonyl chloride
Chemical Formula: $C_8H_8ClNO_3S$
Molecular Weight: 234

Sodium Hydroxide
Chemical Formula: HNaO
Molecular Weight: 40.00

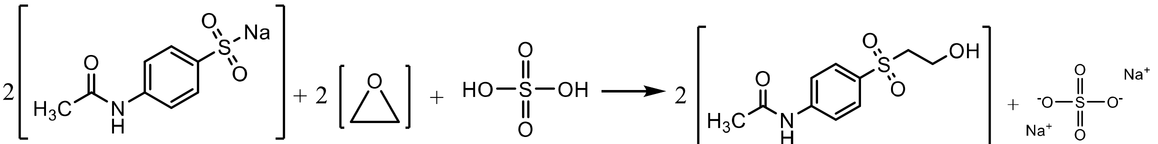
Sodium Bisulphite
Chemical Formula: $HNaO_3S$
Molecular Weight: 104.05

4-acetamidophenyl sulfonyl sodium
Chemical Formula: $C_8H_8NNaO_3S$
Molecular Weight: 221.21

Sodium Sulphate
Chemical Formula: Na_2O_4S
Molecular Weight: 142.04

Sodium Chloride
Chemical Formula: ClNa
Molecular Weight: 58.44

2. Ethoxylation



4-acetamidophenyl sulfonyl sodium
Chemical Formula: $C_8H_8NNaO_3S$
Molecular Weight: 221.21

Ethylene Oxide
Chemical Formula: C_2H_4O
Molecular Weight: 44.05

Sulphuric Acid
Chemical Formula: H_2O_4S
Molecular Weight: 98.07

2-[(4-acetamidophenyl)sulfonyl]ethyl hydroxide
Chemical Formula: $C_{10}H_{13}NO_4S$
Molecular Weight: 243.28

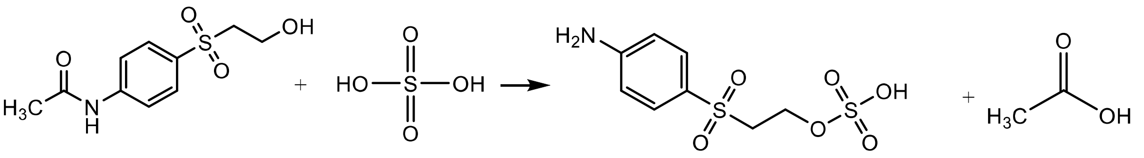
Sodium Sulphate
Chemical Formula:
Na_2O_4S
Molecular Weight: 142.04

Ethylene Oxide
Chemical Formula: C_2H_4O
Molecular Weight: 44.05

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

Ethylene Glycol
Chemical Formula: $C_2H_6O_2$
Molecular Weight: 62.07

3. Esterification



2-[(4-acetamidophenyl)sulfonyl]ethyl hydroxide
Chemical Formula: $C_{10}H_{13}NO_4S$
Molecular Weight: 243.28

Sulphuric Acid
Chemical Formula: H_2O_4S
Molecular Weight: 98.07

2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate
Chemical Formula: $C_8H_{11}NO_6S_2$
Molecular Weight: 281.30

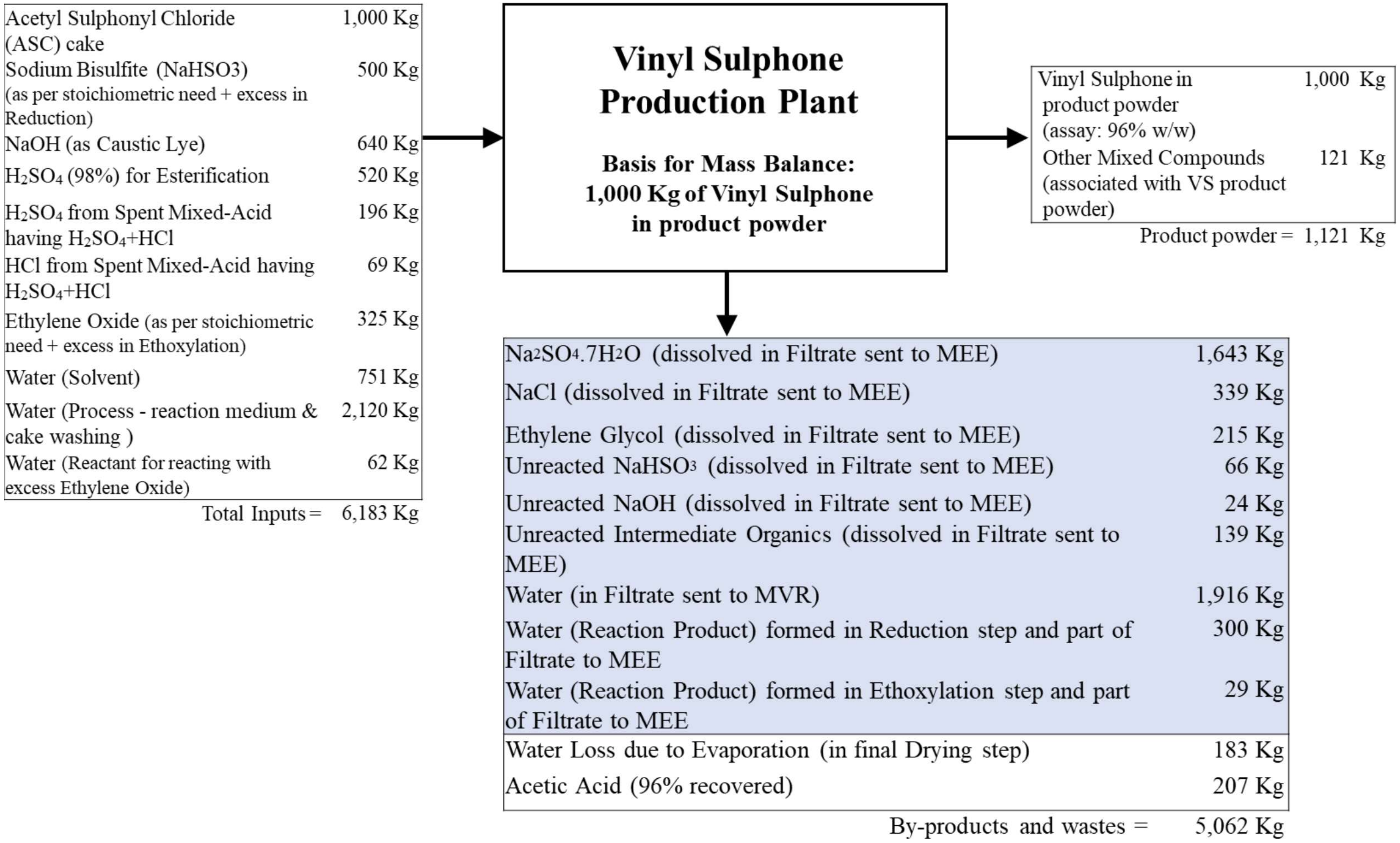
Acetic Acid
Chemical Formula: $C_2H_4O_2$
Molecular Weight: 60.05

With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant “as a production unit” is presented in **Figure 1.6**; with the basis of 1 Ton production of Vinyl Sulphone at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of Vinyl Sulphone synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing Vinyl Sulphone molecule is elaborated in this analysis. **Table 1.6** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of Vinyl Sulphone at Bodal Unit VII. As presented in the Table, 1 Ton of Vinyl Sulphone production also produces 267 Kg of Water (as a by-product). This water, however, remains mixed with the bulk of the reacting mass in the reactor and eventually gets removed downstream through one or more unit operations.

Critical Discussion on the Water Budget: Further, **Table 1.7** depicts the detailed 'Water Budget' for production of one Ton of Vinyl Sulphone at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the Vinyl Sulphone production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 3.2 Ton per Ton of Vinyl Sulphone production. More importantly, Table 1.7 also elaborates on all the efforts of reuse and recycle of the recovered water within the process plant. Because of these efforts, a substantial quantity of water is being saved and reused (2.833 Ton of water per Ton of Vinyl Sulphone production). This is the high point in process innovation – because of which nearly 88% water is being recycled.

In summary, the net freshwater requirement works out to be 0.367 Ton of water per Ton of Vinyl Sulphone production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of moisture associated with product cake, solid waste disposed of in CHW-TSDF or sent to cement industries as well as on account of evaporation losses (see Table 1.7).



Acetyl Sulphonyl Chloride (ASC) cake	1,000 Kg
Sodium Bisulfite (NaHSO3) (as per stoichiometric need + excess in Reduction)	500 Kg
NaOH (as Caustic Lye)	640 Kg
H_2SO_4 (98%) for Esterification	520 Kg
H_2SO_4 from Spent Mixed-Acid having H_2SO_4+HCl	196 Kg
HCl from Spent Mixed-Acid having H_2SO_4+HCl	69 Kg
Ethylene Oxide (as per stoichiometric need + excess in Ethoxylation)	325 Kg
Water (Solvent)	751 Kg
Water (Process - reaction medium & cake washing)	2,120 Kg
Water (Reactant for reacting with excess Ethylene Oxide)	62 Kg
Total Inputs =	6,183 Kg

Vinyl Sulphone Production Plant

Basis for Mass Balance: 1,000 Kg of Vinyl Sulphone in product powder

Vinyl Sulphone in product powder (assay: 96% w/w)	1,000 Kg
Other Mixed Compounds (associated with VS product powder)	121 Kg
Product powder =	1,121 Kg

$Na_2SO_4.7H_2O$ (dissolved in Filtrate sent to MEE)	1,643 Kg
NaCl (dissolved in Filtrate sent to MEE)	339 Kg
Ethylene Glycol (dissolved in Filtrate sent to MEE)	215 Kg
Unreacted $NaHSO_3$ (dissolved in Filtrate sent to MEE)	66 Kg
Unreacted NaOH (dissolved in Filtrate sent to MEE)	24 Kg
Unreacted Intermediate Organics (dissolved in Filtrate sent to MEE)	139 Kg
Water (in Filtrate sent to MVR)	1,916 Kg
Water (Reaction Product) formed in Reduction step and part of Filtrate to MEE	300 Kg
Water (Reaction Product) formed in Ethoxylation step and part of Filtrate to MEE	29 Kg
Water Loss due to Evaporation (in final Drying step)	183 Kg
Acetic Acid (96% recovered)	207 Kg
By-products and wastes =	5,062 Kg

Figure 1.6 Input-output analysis of Vinyl Sulphone at Bodal Unit VII (Basis: 1,000 Kg of Vinyl Sulphone product powder)

Table 1.6 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of Vinyl Sulphone at Bodal Unit VII

Role of Water in the Process Plant	Quantity per Ton of Vinyl Sulphone production (Kg)
Water (as Reactant) for reacting with excess Ethylene Oxide	62
Water (Reaction Product) formed in Reduction step & accounted for in filtrate sent to MEE	-300
Water (Reaction Product) formed in Ethoxylation step & accounted for in filtrate sent to MEE	-29
Net Water Consumption (in reactive steps) =	**-267** *

* 267 Kg of water is generated during production of one Ton of Vinyl Sulphone.

Table 1.7 A detailed 'Water Budget' for production of one Ton of Vinyl Sulphone at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the Vinyl Sulphone production plant.

Role of Water in the Process Plant	**Quantity per Ton of Vinyl Sulphone production (Kg)**
Input of Water (Basis: 1 Ton of Vinyl Sulphone)	
Water (Solvent)	813
Water (Process - cake washing)	2,120
Water generated in several reactive steps	267
Total input of water for one Ton of Vinyl Sulphone =	**3,200**
Emission of Water (Basis: 1 Ton of Vinyl Sulphone)	
Water recovered as Condensate from MEE	-2,112
Reused and recycled water as Condensate from MEE	2,112
Water of crystallization (Glauber's salt, $Na_2SO_4.7H_2O$) output of Crystallizer	-721
Indirect water recycling due to reuse of Glauber's salt in the process	721
Water lost in Spray Drying	-184
Water Loss due to Evaporation	-183
Total input of water for one Ton of Vinyl Sulphone =	**-3,200**
Condensate Water reused from various sources	**2,833**
Water leaving the system (associated with solids & evaporation loss)	**-367**
Net freshwater requirement (3,200 – 2,833 = 367)	**367**

<u>Critical Discussion on Spent Mixed-Acid</u>: It was reported to IIT Bombay team that the Spent Mixed-Acid generated from the Drowning step in ASC production is stored and reused as per the requirements in the Vinyl Sulphone production plant as well as in the H-Acid production plant. A smaller portion is reused in Ethoxylation step in Vinyl Sulphone production process and a larger portion is added to the Isolation step in H-Acid production process.

As per the detailed mass balance performed in this study, on an average, the composition and the corresponding concentrations of the constituents in the Spent Mixed-Acid is estimated (with the help of Figure 1.5 and Table 1.4 and Table 1.5) and presented in **Table 1.8**.

Table 1.8 The approx. composition and concentration of the Spent Mixed-Acid generated from the Drowning step in the ASC production process along with estimation of COD of the Spent Mixed-Acid. It was reported to IITB by Bodal Unit VII that the entire quantity of Spent Mixed-Acid generated during production of ASC is reused in the production of H-Acid and Vinyl Sulphone (captive consumption).

Polluting Constituent	**Weight (Kg) per Ton ASC in Spent Mixed-Acid**	**Volume of Spent Mixed-Acid (L) per Ton of ASC production**	**Concentration of the polluting compound (mg/L)**	**Theoretical COD (mg/L)**
Acetanilide	59.35	3,306	17,950	57,368
Acetyl Sulphonyl Chloride (ASC)	4.75	3,306	1,437	1,861
Sulphanilic Acid	20.55	3,306	6,217	18,952
Acetic Acid	7.12	3,306	2,154	2,297
Total estimated COD (mg/L) =				80,478

It was reported to IITB by Bodal Unit VII that the entire quantity of Spent Mixed-Acid generated during production of ASC is reused in the production of H-Acid and Vinyl Sulphone (captive consumption). The ASC production data were not revealed to IITB team by Bodal Unit VII. As a result, the exact quantum of Spent Mixed-Acid generated in production of ASC for the sister-concern of Bodal Unit VII (production for non-captive use) could not be estimated in the mass balance exercise. However, the quantum of acid generated from 1 Ton of ASC is presented in Figure 1.5 and Table 1.8.

As indicated in the Table, the overall Chemical Oxygen Demand (COD) of the Spent Mixed-Acid works out to be 80,478 mg/L. It is important to notice the major constituents of Spent Mixed-Acid and their corresponding contributions to COD of the Spent Acid are carefully estimated and depicted in Table 1.8. By no stretch of imagination, can the Spent Mixed-Acid having several organic pollutants (COD of 80,478 mg/L) can be referred to as a"dilute stream".

Clearly, as suggested by Table 1.8, rather huge quantities of pollutants, *namely*: Acetanilide, Acetyl Sulphonyl Chloride (ASC), Sulphanilic Acid, estimated as 141, 11, and 48 Ton per year, respectively, are sent to the landfill in the authorized CHW-TSDF. These compounds make up about 20% of the total weight of the ash sent to the landfill – the other 80% consists of inorganic salts.

It is the considered opinion of the author of this report that targeted R&D must be undertaken to reduce the concentration of organics in the Spent Mixed-Acid through major process innovation in the ASC / Vinyl Sulphone production process. In absence of such intervention, huge quantities of polluting compounds (or their derivatives) will end up in the Spray Dryer ashes generated in H-Acid as well as Vinyl Sulphone production plants. It is worrisome that such toxic compounds will be eventually landfilled in CHW-TSDF.

1.7 Gap Analysis for Vinyl Sulphone Production

Gap refers to the space between "where we are" (the present state) and "where we want to be" (the target state). A gap analysis may also be referred to as a needs analysis, needs assessment or ***Need-Gap Analysis***.

The first step in conducting the so-called *Need-Gap Analysis* is to establish the specific target objectives by looking at the company's immediate and long-term interest (mission statement, strategic goals and improvement objectives). The next step is to analyse current business processes by collecting relevant data on performance levels and how resources are presently allocated to these processes. This data can be collected from a variety of sources depending on what is being analysed. For example, by looking at the documentation, conducting interviews with the experts and production managers, brainstorming and observing the production process. Lastly, after comparing the company's current state against the desirable and mandatory environmental as well as work-place safety requirements; a comprehensive plan can be developed. Such "plan" outlines the specific steps to take to fill the gap between its current and future states, and reach its target objectives.

Small and medium scale industries, in particular, can benefit from performing such *Need-Gap Analysis*. Such analysis could have the following THREE target objectives:

1. How to allocate resources?,
2. How to improve performance and profits? and
3. How to improve work-place safety and minimize environmental pollution loads?

In the following section, an effort has been made to present the improvements for short-term benefits as well as long-term benefits; based on the methodology described above.

Improvements for Short-Term Benefits

Improvement of Scrubber Performance in Chlorosulphonation Step: The Chlorosulphonation Step consists of two sub-steps, namely, reaction with Chlorosulphonic Acid and reaction with Thionyl Chloride. The first sub-step results in the formation of HCl gas, and the second sub-step results in the formation of a mixture of acidic gases (having more of HCl gas and less of SO_2 gas). It is well known that these acidic gases are highly corrosive in nature, hence, scrubbing them off would be necessary. The scrubbing results in the formation of by-products which are either reused or sold off.

Currently, in Bodal Unit VII, a system of three-stage packed bed scrubbers is employed for ensuring minimization of air pollution. The HCl gas is scrubbed with two-stage counter-current water scrubber resulting in the generation of dilute HCl solution (~30% concentration). Subsequently, in the third stage of scrubber-system, the flue gas (now free from HCl fumes) is subjected to one-stage scrubbing with dilute NaOH solution to absorb the SOx (mostly SO_2) – before venting off. Thus, scrubbing of SO2 with dilute NaOH solution results in the generation of dilute Sodium Bisulphite solution.

The maximum concentration from the packed bed scrubber for HCl solution is typically around 25 – 30%. A 'Falling Film Absorber' employed in place of the two-stage counter-current packed bed absorber (currently used in Bodal Unit VII) can, in fact, increase the resulting concentration of the dilute HCl solution to 35 – 37%.

Typically, 'Falling Film Absorber' has multiple advantages over packed bed scrubber:

a. It requires less space,

b. it is more efficient,

c. it has a lower pressure drop,

d. it operates at lower temperatures, and

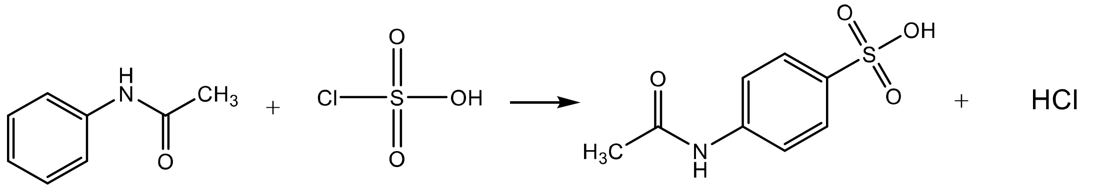
e. it has higher efficiency.

Thus, the targeted R&D must be performed to evaluate the relative benefits of using the 'Falling Film Absorber' in place of the current scrubbing system.

Significance of Minimization of Water Used in Drowning Step: In the Chlorosulphonation step, Acetanilide is slowly added to Chlorosulphonic Acid already present in the reactor. The first substitution in acetanilide molecule is of Sulphonic group in place of Hydrogen (Step 1). During this step, HCl gas is generated. The second substitution occurs in Acetyl Sulphonic Acid when Thionyl Chloride is added to the reacting mass (*i.e.* Chlorination; Step 2). This leads to the evolution of HCl and SO_2 gases from the reacting mass.

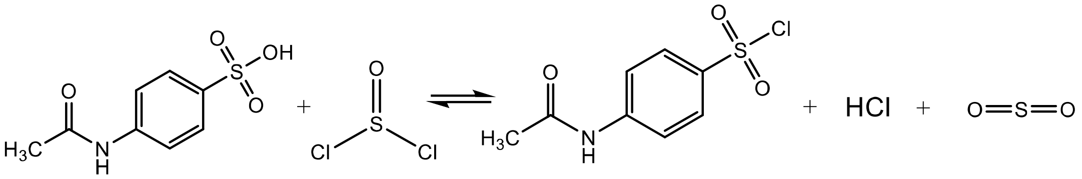
The reactions in the Chlorosulphonation step are summarized below:

Step 1: Sulphonation of Acetanilide



Acetanilide	Chlorosulphonic Acid	4-Acetamidobenzenesulfonic Acid	Hydrochloric Acid
Chemical Formula: C_8H_9NO	Chemical Formula: $ClHO_3S$	Chemical Formula: $C_8H_9NO_4S$	Chemical Formula: ClH
Molecular Weight: 134	Molecular Weight: 117	Molecular Weight: 215	Molecular Weight: 36

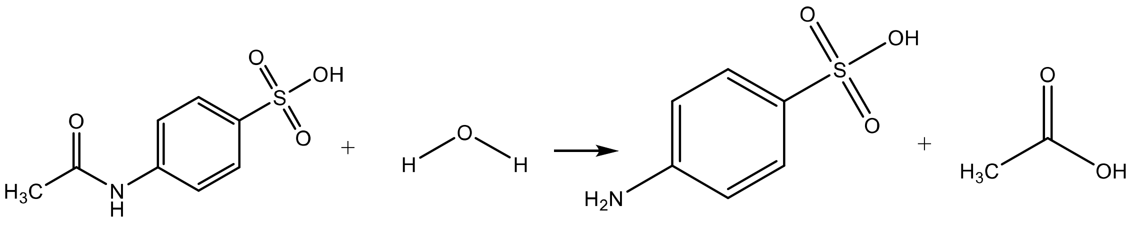
Step 2: Chlorination of Acetyl Sulphonic Acid



4-Acetamidobenzenesulfonic acid	Thionyl Chloride	4-Acetamidobenzenesulfonyl chloride	Hydrochloric Acid	Sulphur Dioxide
Chemical Formula: $C_8H_9NO_4S$	Chemical Formula: Cl_2OS	Chemical Formula: $C_8H_8ClNO_3S$	Chemical Formula: ClH	Chemical Formula: O_2S
Molecular Weight: 215	Molecular Weight: 119	Molecular Weight: 234	Molecular Weight: 36	Molecular Weight: 64

It is important to note that the Sulphonation step in Chlorosulphonation is exothermic. Furthermore, the Chlorination step in Chlorosulphonation is an equilibrium reaction with the forward reaction being exothermic and reverse reaction being endothermic. Clearly, molecular conversion to 4-Acetamidobenzenesulfonyl chloride or more commonly known as 'Acetyl Sulphonyl Chloride' (the desired product in Chlorosulphonation process) would maximize only when the exothermic heat is removed from the reacting mass as quickly as possible.

The low temperature thus favours the reverse reaction forming Acetyl Sulphonic Acid. This Acetyl Sulphonic Acid then reacts with water, which is abundantly present, to then form Sulphanilic Acid. The Sulphanilic Acid thus formed is taken out with the filtrate which is actually the Spent Mixed-Acid. This is a major contributor to the Chemical Oxygen Demand (COD) of the Spent Mixed-Acid, and since it is recycled to the Isolation stage in H-Acid, it forms byproducts there as well thus, in turn, increasing the COD load in the H-Acid production process. The reaction showing the formation of Sulphanilic Acid is shown below:



4-Acetamidobenzenesulfonic acid
Chemical Formula: $C_8H_9NO_4S$
Molecular Weight: 215

Water
Chemical Formula: H_2O
Molecular Weight: 18

Sulphanilic Acid
Chemical Formula: $C_6H_7NO_3S$
Molecular Weight: 173

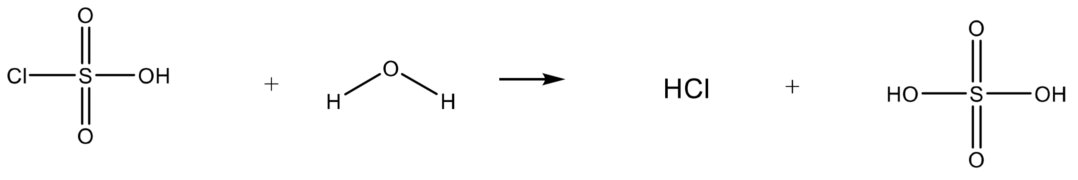
Acetic acid
Chemical Formula: $C_2H_4O_2$
Molecular Weight: 60

Reportedly, at Bodal Unit VII, the 'Cooling Step' is performed to arrest the reactions by dumping the product mass of Chlorosulphonation step on a mixture of ice and water in another vessel (conventionally referred to as 'Drowning Step') to achieve the following two benefits:

a. temperature can be decreased quickly with the help of a mixture of ice and water (the desired temperature is 15-20°C) and

b. the resulting net water addition to the reactor also helps in improving the workability of the reaction mixture; since the product mass formed in Chlorosulphonation process is a slurry and it is difficult to pump and work with.

Unfortunately, the addition of ice and water in the 'Drowning' step described above creates the possibility of the reaction of water with unreacted Chlorosulphonic Acid in the reaction mass. It is interesting to note that Chlorosulphonic Acid reacts violently with water exothermically and forms HCl and SO_2 gases. However, at this point, the reacting mass has enough water present in the reactor at the end of drowning step and formation of aqueous H_2SO_4 happens more eminently (instead of getting SO_2 gas out from the reacting mass). This reaction is depicted below:



Chlorosulphonic Acid
Chemical Formula: $ClHO_3S$
Molecular Weight: 117

Water
Chemical Formula: H_2O
Molecular Weight: 18

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36

Sulphuric Acid
Chemical Formula: H_2O_4S
Molecular Weight: 98

Clearly, the addition of mixture of ice and water in the Drowning step leads to one undesirable complication – which is the generation of exothermic heat in the reaction mass due to the reaction of added water with unreacted Chlorosulphonic Acid, as explained above. Thus, the overall temperature increase of reacting mass becomes detrimental to the yield of Chlorosulphonation process. However, the benefit of the reaction of Chlorosulphonic Acid with water “removes” the excess unreacted acid from the reaction mass and thus rules out the possibility of the formation of any exothermic heat in the following unit processes (downstream of the Chlorosulphonation step).

In sum, the exothermic reactions in Chlorosulphonation process (i.e. Steps 1 and 2) are desirable. But, it is not easy to decide whether the exothermic reaction of added water with unreacted Chlorosulphonic Acid is desirable or otherwise. Indeed, it is desirable because one would want to remove the unreacted Chlorosulphonic Acid from the reaction mass and the resulting exotherm is undesirable because it favours degradation of the product! Moreover, Ice melts and forms water which not only increases the effluent load but also causes further exothermicity due to the reaction of Chlorosulphonic Acid with water.

It is in this context that a better unit operation needs to be devised to perform the so-called ‘Cooling Step’ rather than simply employ the conventional ‘Drowning Step’. In fact, these complex reactions in Chlorosulphonation process make the Vinyl Sulphone production rather tricky!

As mentioned above, although addition of water is an unavoidable step in order to increase workability. But the fact that ‘Water is a Universal Solvent’ is both beneficial and deleterious in this case. Moreover, it is an enormous task to treat the effluent generated in these steps. Although it is mostly H_2SO_4 mixed in with other by-products / side products and water, the concentration of H_2SO_4 is heavily diluted if more water is used. Following efforts can be made in order to minimize water consumption:

A possible improvement to this step can be the use of jacketed vessel (or reactor) cooled by “chilled brine” for cooling the mass instead of dumping the mass on ice and water. However, it is important to perform a targeted R&D to report before implementing the suggestion.

Ice melts and forms water which not only increases the effluent load but also causes further exothermicity due to the reaction of Chlorosulphonic Acid with water. Thus, switching to using Brine cooling instead of ice has dual benefits; which are, a significant drop in the effluent generation and faster and more efficient cooling hence taking care of the exothermicity.

The highly exothermic reaction of Chlorosulphonic Acid with the added water, as seen above, leads to the formation of HCl and H_2SO_4 dissolved in solution. This is over and above the amount of generated HCl in the previous Chlorosulphonation step. The shortcoming here is that due to the presence of excess of water, the generated HCl tends to get absorbed in the acidic "drowned" solution. This results in the formation of a mixture of HCl and H_2SO_4 solution. This may be problematic for two reasons:

a. The presence of HCl along with the reaction mass could cause unnecessary hindrances and may lead to the formation of some fraction of unwanted products.

b. The H_2SO_4 solution generated from this step is intended to be reused as 'spent acid' in Vinyl Sulphone as well as H-Acid processes.

It is reported in literature that the use of **cold H_2SO_4 solution (typically 40%)** with very limited water before the Drowning step (Note: more water can always be added if flowability is an issue). It would be beneficial to adjust the concentration of the added cold H_2SO_4 such that there is only a small molar excess of water than what is required to decompose Chlorosulphonic Acid to prevent the solution from becoming too dilute and formation of undesired by-products such as Sulphanilic Acid. The cold H_2SO_4 is added since the decomposition reaction of Chlorosulphonic Acid is highly exothermic. Thus, not only will the cooling load on the brine system will be reduced due to the intermediate cooling provided by contacting with the cold H_2SO_4 solution, but the amount of ice and water used in the subsequent 'Drowning' step will also be significantly reduced.

The Chlorosulphonic Acid breaks down to form H_2SO_4 and HCl. This is where the situation gets particularly tricky since HCl forms an azeotrope with water making it all the more difficult to separate, especially at lower concentrations. It is well-known that H_2SO_4 is hygroscopic, thus preventing complete dissociation and dissolution of HCl into the water. As a result, HCl gas will be liberated and a much more concentrated H2SO4 solution will be obtained. The HCl gas liberated will need to be scrubbed using appropriate technology. The concentration of H_2SO_4 solution (Spent Mixed-Acid) with the current systems is about 25-30% w/w. With the newly recommended systems in place (*i.e.* jacketed brine cooling and using cold 40% H2SO4 solution), it is reported in literature that the concentration of H_2SO_4 solution can reach up to 55% w/w.

In sum, not only will the use of water in the Drowning step be reduced substantially but the recovered H_2SO_4 solution will be of a much higher concentration making its handling easier in the plant.

The targeted R&D, thus, will need to be performed in order to evaluate the application of the 'chilled brine' cooling technology in the Drowning step, as well as the technique of 'contacting the reaction mass with cold H_2SO_4 before the Drowning step'. In the 'Big Picture' point of view, these measures are necessary to reduce the pollution which is currently, in fact, being carried forward to other reactors and processes as well.

Improved Process of Unloading Ethylene Oxide from Tanker to the Storage Tank: The current method of transferring Ethylene Oxide from tanker to storage tank involves use of Nitrogen gas for pressure management, and water for dilution of gases. This could lead to a huge loss of Ethylene Oxide as a result of possible leaks. It is reported in literature that the loss of Ethylene Oxide per tanker over a month is estimated to be around 100 Kg in monsoon and about 300 Kg in summer. The hazard of working with Ethylene Oxide is well-known – it explodes instantaneously on contact with oxygen. Hence, leakage is a major concern from a health and safety point of view.

A possible improvement to the current process is the use of centrifugal pump to transfer Ethylene Oxide from the tanker to storage tank and a condenser to recover the Ethylene Oxide vapours. This not only eliminates the need for use of any inert gas for the transferring process but also eliminates the chance of any effluent generation. Thus, it is possible to significantly reduce the environmental load while also increasing safety in the facility. Although it will be a much more sophisticated apparatus to set up and operate, the positives are far too many to discourage this process enhancement.

Thus, trials must be conducted to determine the suitability of using a centrifugal pump to transfer Ethylene Oxide from the tanker to storage tank and a condenser to recover the Ethylene Oxide vapours.

Significance of Digital Flowmeters to Track Water Usage: As seen in the water budget, production of H-Acid and VS is highly water-intensive. Keeping a track of water at every input and the output is essential from the point of view of having an accurate water balance and water budget. Currently, since there is no flow meter to keep track of the water usage, the values of the water usage are rough estimates. This is unacceptable. In order to have a perfect mass balance and water balance, every part of the water used in the plant needs to be tracked.

Therefore, the use of digital flowmeters at all the places in the plant where water is used is recommended. The planning and implementation of this recommendation should be expedited and taken up as the first priority.

Housekeeping and Maintenance: The investigation team from IIT Bombay visited this plant several times and discussed with persons from Production and Environment Protection teams. There was a great cooperation from these persons and the information was furnished efficiently through emails, completing the requested tabulated information, cooperating with the personnel from Vadodara Enviro Channel Limited (VECL) while collecting samples and obtaining data as well as through face-to-face interactions during the site visits. The IIT Bombay team is grateful to the company for their help and facilitation.

Frankly, whenever IIT Bombay team visited the production facility as well as ETP and STP, *prima facie* it appeared as though the overall upkeep and housekeeping was visibly poor. Most of the floors and surfaces inside the roof and columns of the shed were unclean, rusted and it was clear that the housekeeping related functions were generally given a low priority.

It is generally understood that the functions related to routine maintenance of equipment, reactors, piping, loading-unloading platforms, and staircases (ladders) become difficult and the overall surroundings have poor housekeeping. It is also understood that the frequency of maintenance, too, increases in the midst of unclean surroundings (more corrosion, frequent breakdown, difficulty in repairs and maintenance).

More importantly, the propensity for accidents, fire, explosion, injury at the workplace are generally found to enhance in the situations where overall maintenance and housekeeping is poor. The modern safety science, in fact, has been lately recommending for superlative interventions related to cleanliness, daily upkeep, and above all, the “preventive maintenance”.

Maintenance and calibration of all instrumentation and control hardware is of utmost importance, not only from the point of view of the production process and product purity but also from the point of view of minimization of pollution and enhancement of health and safety of the workers. Poorly or rarely calibrated instrumentation and control hardware will often lead to the addition of an incorrect amount of inputs to the reactor or give a false picture of the conditions in the reactor. This might, in turn, impact the indoor air quality, safety of the workers, and generation of pollution from the production plant. If the production plant is not properly maintained, the probability of malfunctioning of the instrumentation and process control devices would increase. Also, the functioning of ETP and STP will get affected beyond the certain extent of negligence in the production plant.

In sum, it is well-known that the Vinyl Sulphone production process is extremely complicated and rather highly polluting. No wonder, several states in India and several countries in the world have imposed a ban on the production of these dye-intermediates. Because the raw materials and intermediates involved in the production of Vinyl Sulphone are extremely reactive and corrosive; the maintenance routine should be commensurate with the propensity of rusting and evolution of fumes in the process plant. Clearly, poor maintenance and upkeep could generate an unsafe work environment and pose higher risk to the workers' safety and environment. In addition to this, safety devices such as relief valves, process control equipment, pressure relief valves, etc. must be maintained and replaced as per the industry standards and the best-recommended practices.

The investigation team from IIT Bombay has taken a serious note of these facts and would recommend rather strongly that the housekeeping and maintenance should be improved remarkably in the nearest future. Adequate Personal Protective Equipment (PPE), uniform for all personnel, labelling of equipment, tanks and pipelines should be taken up as the first priority and serious efforts should be made to create the positive first impression.

Constructing a New and Robust Stormwater Collection and Treatment System: The investigation team from IIT Bombay visited Bodal Unit VII multiple times and has taken note of the fact that the stormwater collection system is inadequate in its current installation. Bodal Unit VII produces H-Acid and Vinyl Sulphone. It is a well-known fact Vinyl Sulphone is a complex molecule and the final product is a powder which is soluble in water. This property of Vinyl Sulphone is the primary reason that the stormwater runoff from the Vinyl Sulphone plant and its surrounding areas will more exhibit a high amount of COD even at lower concentrations. This runoff, when combined with the runoff from the surrounding areas of the H-Acid plant, will have a bluish-black colour and significant COD.

A new stormwater drainage system should be constructed which will adequately intercept the surface water and stormwater runoff as per industry standards and divert the water to the ETP for treatment. Since the stormwater from this industry will have COD contributed by highly recalcitrant organic compounds, under no condition should the surface water runoff and/or stormwater runoff be let off into the channel or the environment without treatment in the ETP first. Hence, a new and robust stormwater collection and treatment system must be constructed to intercept and treat the stormwater and surface water runoff as per industry standards. This endeavour must be taken up as the first priority.

Improvements for Long-Term Benefits

Use of Oleum in Chlorosulphonation: According to one recently published Chinese patent (2019), the selectivity of sulphonation at para position of Acetanilide ring can be markedly improved by the use of Oleum (*i.e.* fuming Sulphuric Acid, $H_2SO_4 \cdot SO_3$) as the sulphonation agent. Currently in Bodal Unit VII, Sulphonation of Acetanilide conducted in presence of excess Chlorosulphonic Acid. Instead, according to the patent, if Oleum is used in conjunction with Chlorosulphonic Acid in the ratio 3 to 4:1; the selectivity of sulphonation at para position of Acetanilide ring will improve the yield on one hand and the excess Chlorosulphonic Acid can be saved.

Clearly, through this modification, not only Chlorosulphonic Acid can be saved, but the subsequent reactions of Chlorosulphonic Acid with water and other by-products and wastages can be minimized. Also, the subsequent ratio of H_2SO_4:HCl in the resulting spent mixed-acid will alter in the event of use of Oleum.

The targeted R&D, therefore, will need to be conducted to evaluate the relative benefits of increased selectivity by using Oleum and subsequent changes in mass balance as well as cover the costs of purchasing the patent.

Modification of the Chlorosulphonation Reactor Vessel: According to one recently published Chinese patent (2018), the efficiency of Chlorosulphonation can be drastically improved by certain modifications to the Chlorosulphonation Reactor Vessel. Since the Chlorosulphonation reaction is an equilibrium reaction, it is well-known that an excess amount of Chlorosulphonic Acid must be added to ensure completion of the reaction. This leads to an unreacted fraction of Chlorosulphonic Acid, which later forms Sulphuric Acid and Hydrochloric Acid in the Drowning step. Over and above this fact, operating the current system of the Chlorosulphonation Reactor is a skilled art since Chlorosulphonic Acid is highly viscous, and it is reacted with Acetanilide by direct contact. This leads to a long reaction time and a somewhat incomplete reaction since, as seen above in the 'Improvement for Short Term Benefits' section, Sulphanilic Acid is formed in the Drowning step.

These shortcomings can be reportedly reduced by atomizing the Chlorosulphonic Acid and molten Acetanilide and carrying out the operation in the particular Chlorosulphonation Reactor as mentioned in the patent. The patent mentions the presence of a wire mesh made of a certain material which captures the water generated in the reaction, thus preventing the formation of any Sulphanilic Acid due to unreacted Chlorosulphonic Acid. Since the described system prevents the formation of any by-products, it is also reported to have a higher yield compared to the current system.

The targeted R&D, therefore, will need to be conducted to evaluate the applicability of this technology in the Vinyl Sulphone production process, as well as cover the costs of purchasing the patent.

Alternate Production Routes for Cleaner Production: The current method of Vinyl Sulphone production is through the Acetanilide route. From the facts and details as presented in the above sections, it is clear that while this production route gives an impeccable yield of Vinyl Sulphone, it also leads to a high and especially recalcitrant environmental pollution load. 'Environmental Pollution' is generated in the Chlorosulphonation, Drowning, Reduction and Ethoxylation steps in the current Acetanilide-based production route. This means that four out of five unit processes in the current production route contribute to the generation of pollutants which lead to the addition of more unit operations in order to separate, recover or treat them.

Hence, it is of utmost importance to look into alternatives – alternate production routes with different raw materials and certain process modifications – which will lead to a Cleaner Production of Vinyl Sulphone. A brief description of the pollution load generation from each stage is given below:

The Chlorosulphonation and Drowning steps in the current production process are the first and foremost pollution generating steps. The pollutants are gaseous HCl and gaseous SO_2

from the Chlorosulphonation step and dilute spent acid from the Drowning step. The Reduction step currently uses Sodium Hydroxide (NaOH) in the form of lye and Sodium Bisulphite ($NaHSO_3$) for the conversion of nitro group to amino group. This causes generation of salts such as Na_2SO_4, NaCl. Although Na_2SO_4 is recovered later in the Crystallization process, the other salts and unreacted reactants form a mixture of salts which eventually ends up in the landfill after going through multiple unit operations. As mentioned in the previous section, the Ethoxylation step leads to formation of Ethylene Glycol which is a significant contributor to the overall COD of the waste stream as well as of the reactor washing effluent.

Reportedly, according to various patents (European and Chinese) and commercially available processes, alternate production routes for Vinyl Sulphone are currently practised in the world. However, targeted R&D efforts are required to implement them in the existing production process used by Bodal Unit VII. In other words, those innovations will have to be perfected to reach the desired yield of Vinyl Sulphone, as in the Acetanilide-based process. That being said, these production routes have a markedly superior environmental performance on account of not having the Chlorosulphonation and Drowning steps, as well as a catalytic hydrogenation method instead of the current caustic lye and sodium bisulphite method.

Apparently, there are two possible alternatives in the production process of Vinyl Sulphone – which are briefly described below:

1. Reaction of p-nitrochlorobenzene and β-mercaptoethanol followed by Oxidation, Reduction (Catalytic Reduction) and Esterification to obtain Vinyl Sulphone. This step also eliminates the use of Ethylene Oxide which is extremely dangerous to handle.

2. Reaction of Thiophenol and Ethylene Oxide followed by Oxidation, Nitration, Reduction and Esterification to obtain Vinyl Sulphone.

The targeted R&D, therefore, will need to be conducted to evaluate the relative benefits of the alternate processes using different raw materials and the subsequent reduction of the environmental load as well as cover the costs of purchasing the patent.

1.8 Brief Manufacturing Process of β-Naphthol

The brief manufacturing process of β-Naphthol is presented in this section. The brief production process flow diagram of β-Naphthol is given in **Figure 1.7**. The major production process details are given below:

1. Sulphonation
    a. Charge Sulphuric Acid (98%) into the reactor.
    b. Charge Naphthalene in the reactor. The reactor employed for this is a closed jacketed vessel.
    c. Thus, a mixture of 1-naphthalene sulphonic acid and 2-naphthalene sulphonic acid is formed. 2-naphthalene sulphonic acid is the desired product. The reaction mass is sent to the Stripper.
2. Naphthalene Stripper
    a. The reaction mass is charged into the reactor along with live steam and water for breaking down the unwanted product *i.e.* 1-naphthalene sulphonic acid.
    b. Breakdown of 1-naphthalene sulphonic acid leads to the formation of Naphthalene again along with Sulphuric Acid.
    c. The Naphthalene is vaporized along with steam and separated by condensation for use in the subsequent batches.
    d. The reaction mass, now free from 1-naphthalene sulphonic acid and unreacted Naphthalene is then sent to the Neutralization vessel.

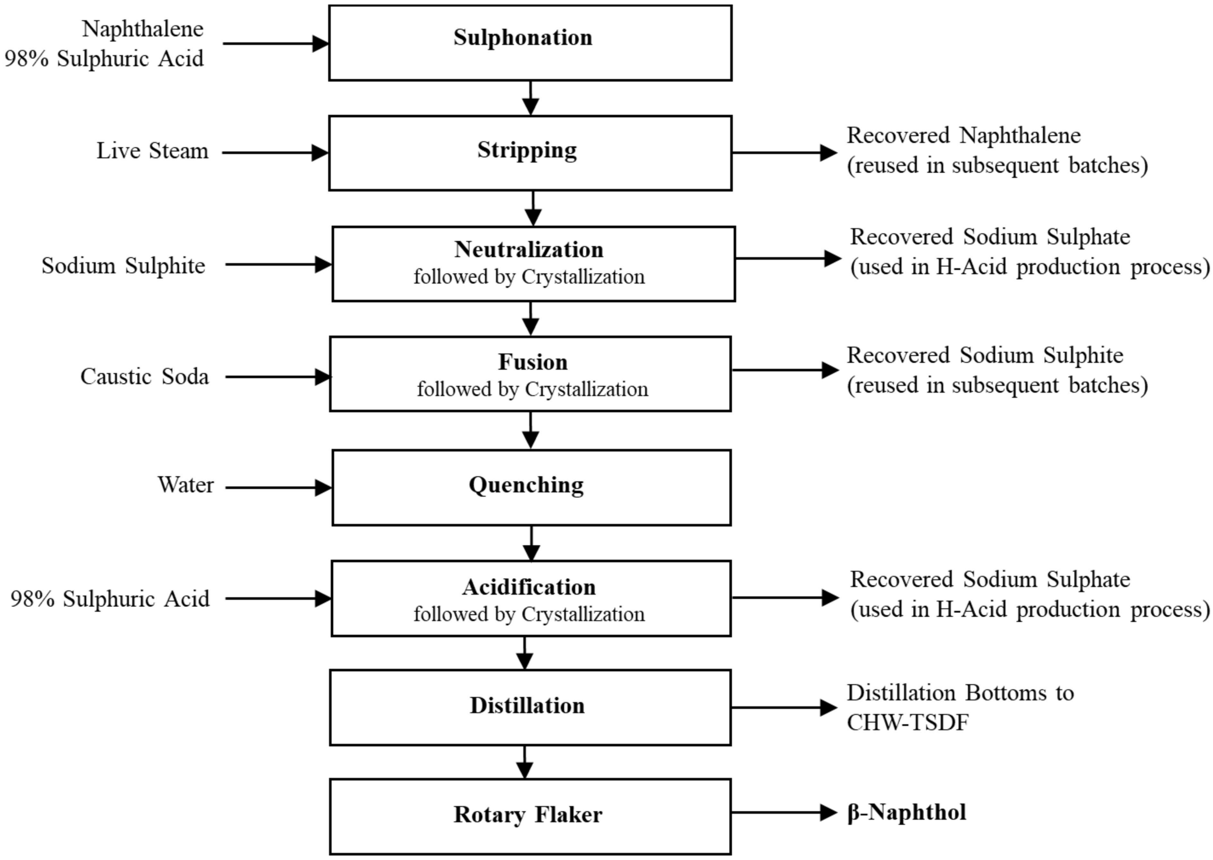


Figure 1.7 Production Process Flow Diagram of β-Naphthol at Bodal Unit VII operated in the batch-wise mode

3. Neutralization

    a. The stripped reaction mass is neutralized with recycled Sodium Sulphite which is a by-product in the production process of β-Naphthol.

    b. During the reaction, SO_2 gas is generated which is circulated in the Acidification reaction vessel of the process.

    c. The neutralized mass now contains the sodium salt of 2-naphthalene sulphonic acid, commonly known as β-salt.

    d. The neutralized mass is sent to the Crystallizer for recovery of Sodium Sulphate which is a by-product of the neutralization of the excess Sulphuric Acid.

4. Quenching

    a. The neutralized mass now free of Sodium Sulphate is Quenched for separation of β-salt.

    b. The reaction mass is then sent to the Caustic Fusion reactor.

5. Fusion

    a. The β-salt is now subjected to Caustic Fusion with Caustic Soda flakes at high temperatures.

    b. Thus, sodium salt of β-Naphthol is formed and Sodium Sulphite is formed as the by-product.

    c. The Sodium Sulphite is separated out by Crystallization and reused in the Neutralization step.

    d. The crude sodium salt of β-Naphthol is then sent to the final reaction step of Acidification.

6. Acidification

    a. The crude sodium salt of β-Naphthol is acidified with Sulphuric Acid.

   b. Along with this, the SO_2 generated in Neutralization step is circulated in this reactor to maintain the desired level of acidity.

   c. Thus, crude β-Naphthol is obtained.

7. Distillation and Rotary Flaker

   a. The crude β-Naphthol is distilled to separate out the water and other by-products at different temperatures to obtain the pure β-Naphthol.

   b. The distillation bottoms are sent to the Tar Pit and finally disposed of at the CHW-TSDF.

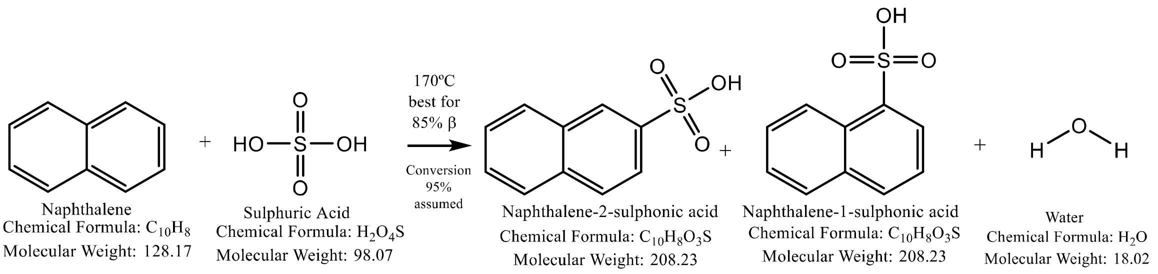
   c. The pure β-Naphthol is then cooled and flakes are formed in the rotary drum flaker.

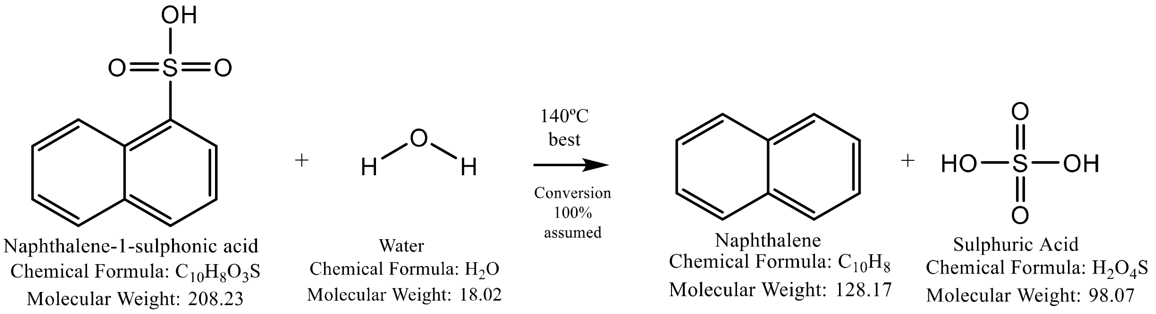
   d. The final product is packed and shipped.

1.9 Stoichiometry and Mass Balance for β-Naphthol Production

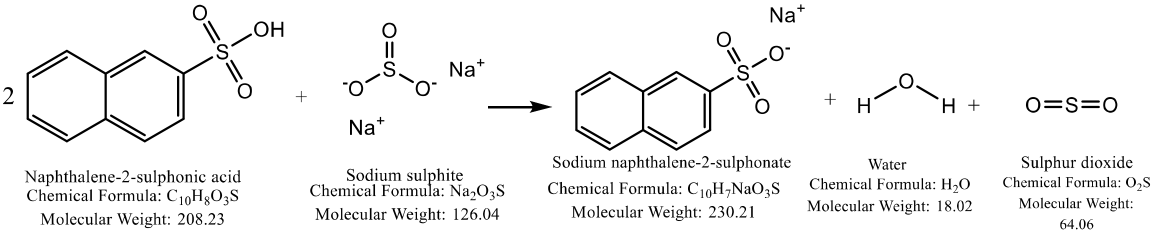
As discussed earlier, Figure 1.7 illustrates the production process flow diagram for β-Naphthol, as practised in the batch-wise production, at Bodal Unit VII. At the outset, all the important reactions performed in the production process of β-Naphthol are briefly presented below:

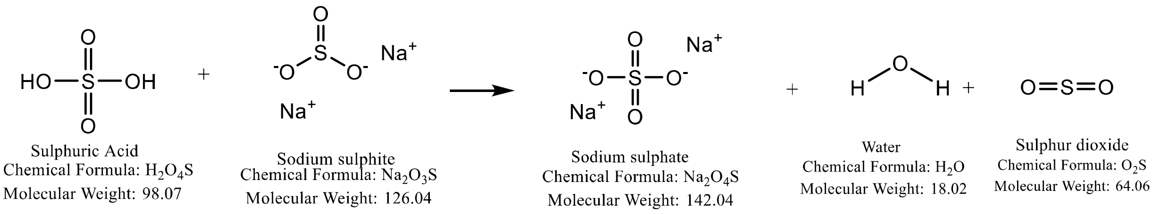
1. Sulphonation



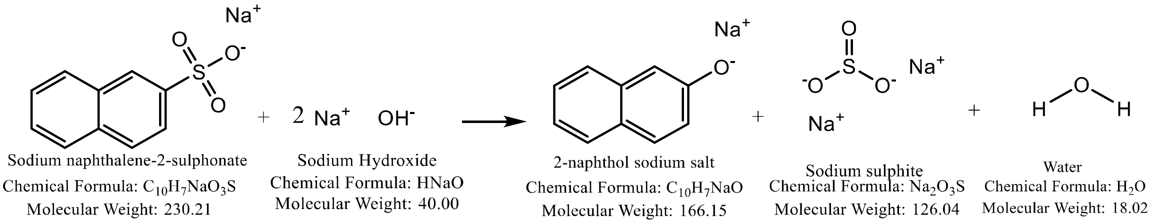


2. Neutralization

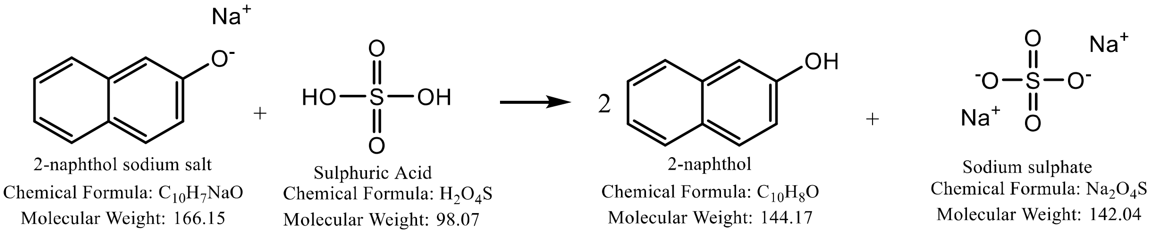




3. Caustic Fusion



4. Acidification



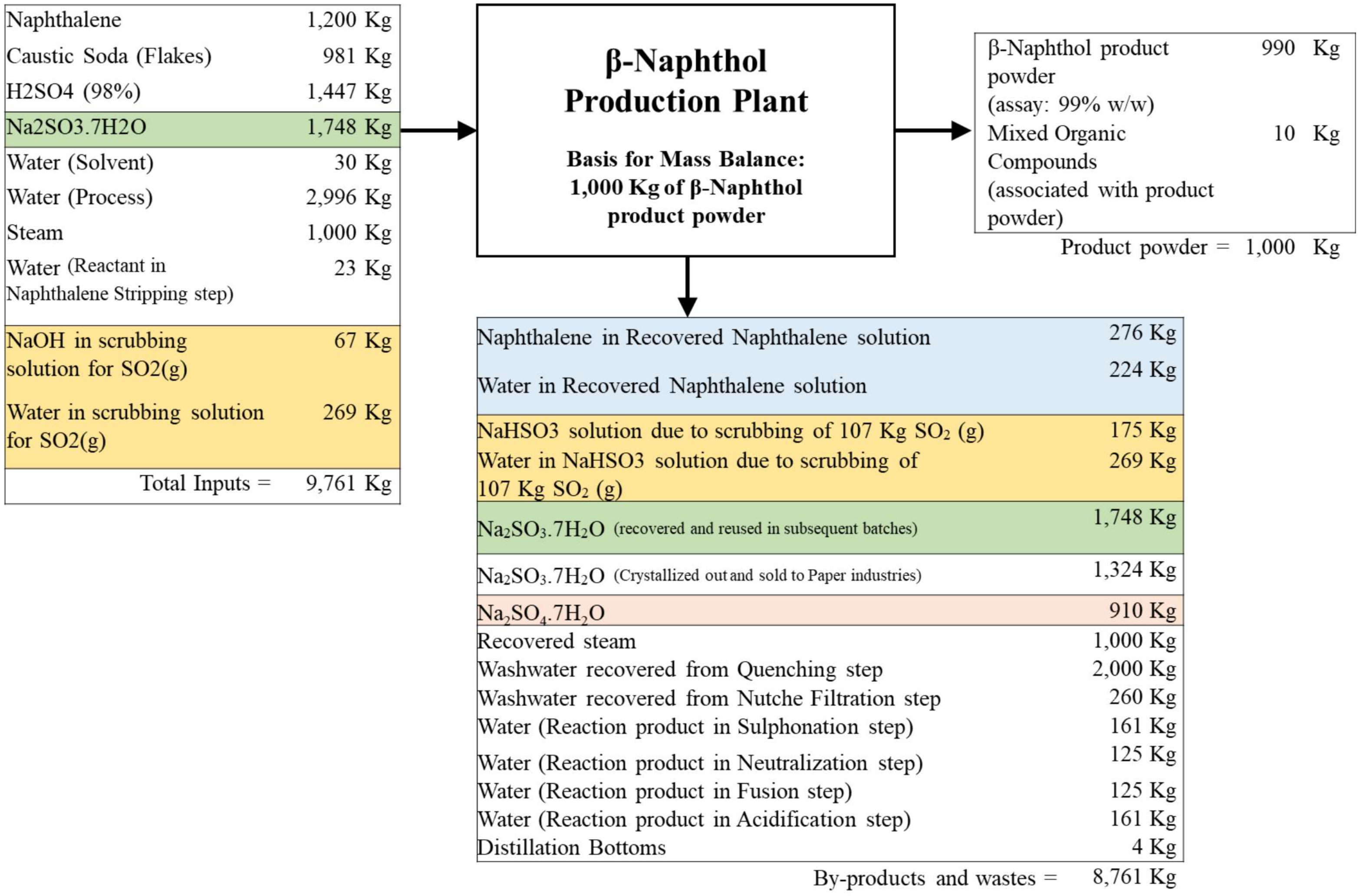
With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant “as a production unit” is presented in **Figure 1.8**; with the basis of 1 Ton production of β-Naphthol at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of β-Naphthol synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing β-Naphthol molecule is elaborated in this analysis. **Table 1.9** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of β-Naphthol at Bodal Unit VII. As presented in the Table, 1 Ton of β-Naphthol production also produces 0.548 Ton of Water (as a by-product). This water, however, remains mixed with the bulk of the reacting mass in the reactor and eventually gets removed downstream through one or more unit operations.

Further, **Table 1.10** depicts the detailed 'Water Budget' for production of one Ton of β-Naphthol at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the β-Naphthol production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 5.448 Ton per Ton of β-Naphthol production. More importantly, Table 1.3 also elaborates on all the efforts of reuse and recycle of the recovered water within the process plant. Because of these efforts, a substantial quantity of water is being saved and reused (5.02 Ton of water per Ton of β-Naphthol production). This is the high point in process innovation – because of which nearly 92% water is being recycled.

In summary, the net freshwater requirement works out to be 0.428 Ton of water per Ton of β-Naphthol production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of moisture associated with product cake, solid waste disposed of in CHW-TSDF or sent to cement industries as well as on account of evaporation losses (see Table 1.3).

In summary, the net freshwater requirement works out to be 0.428 Ton of water per Ton of β-Naphthol production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of moisture associated with by-product cake (see Table 1.10).



Naphthalene	1,200 Kg
Caustic Soda (Flakes)	981 Kg
H2SO4 (98%)	1,447 Kg
Na2SO3.7H2O	1,748 Kg
Water (Solvent)	30 Kg
Water (Process)	2,996 Kg
Steam	1,000 Kg
Water (Reactant in Naphthalene Stripping step)	23 Kg
NaOH in scrubbing solution for SO2(g)	67 Kg
Water in scrubbing solution for SO2(g)	269 Kg
Total Inputs =	9,761 Kg

β-Naphthol product powder (assay: 99% w/w)	990 Kg
Mixed Organic Compounds (associated with product powder)	10 Kg
Product powder =	1,000 Kg

Naphthalene in Recovered Naphthalene solution	276 Kg
Water in Recovered Naphthalene solution	224 Kg
NaHSO3 solution due to scrubbing of 107 Kg SO_2 (g)	175 Kg
Water in NaHSO3 solution due to scrubbing of 107 Kg SO_2 (g)	269 Kg
$Na_2SO_3.7H_2O$ (recovered and reused in subsequent batches)	1,748 Kg
$Na_2SO_3.7H_2O$ (Crystallized out and sold to Paper industries)	1,324 Kg
$Na_2SO_4.7H_2O$	910 Kg
Recovered steam	1,000 Kg
Washwater recovered from Quenching step	2,000 Kg
Washwater recovered from Nutche Filtration step	260 Kg
Water (Reaction product in Sulphonation step)	161 Kg
Water (Reaction product in Neutralization step)	125 Kg
Water (Reaction product in Fusion step)	125 Kg
Water (Reaction product in Acidification step)	161 Kg
Distillation Bottoms	4 Kg
By-products and wastes =	8,761 Kg

Figure 1.8 Input-output analysis of β-Naphthol at Bodal Unit VII (Basis: 1,000 Kg of β-Naphthol)

Table 1.9 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of β-Naphthol at Bodal Unit VII

Role of Water in the Process Plant	**Quantity per Ton of β-Naphthol production (Kg)**
Water (Reactant) in Naphthalene stripping	23
Water (Reaction Product) formed in Sulphonation step	-161
Water (Reaction product in Neutralization step)	-125
Water (Reaction product in Fusion step)	-125
Water (Reaction product in Acidification step)	-161
Net Water Consumption (in reactive steps) =	**-548 ***

* 548 Kg of water is generated during production of one Ton of B-Naphthol .

Table 1.10 A detailed 'Water Budget' for production of one Ton of β-Naphthol at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the β-Naphthol production plant.

Role of Water in the Process Plant	**Quantity per Ton of β-Naphthol production (Kg)**
Input of Water (Basis: 1 Ton of β-Naphthol)	
Water (added as Solvent)	904
Water (generated in reactive steps from the past batch)	548
Water (consumed in several unit operations)	2,996
Water (consumed in generation of Steam)	1,000
Total input of water for one Ton of β-Naphthol =	**5,448**
Emission of Water (Basis: 1 Ton of β-Naphthol)	
Water in recovered Naphthalene solution after Stripping	-224
Recycled Water from recovered Naphthalene solution after Stripping	224
Water of crystallization (Sodium Sulphite, $Na_2SO_3.7H_2O$) output of Crystallizer	-1,536
Indirect water recycling due to reuse of Sodium Sulphite in the process	1,536
Water of crystallization (Glauber's salt, $Na_2SO_4.7H_2O$) output of Crystallizer	-428
Recovered Steam	-1,000
Water (recovered from Quenching step)	-2,000
Water (recovered from Filtration of Sodium Sulphite crystals)	-260
Total emission of water for one Ton of β-Naphthol =	**-5,448**
Condensate Water reused from various sources	**5,020**
Water leaving the system (associated with solids & evaporation loss)	**428**
Net freshwater requirement (5,448 – 5,020 = 428)	**428**

1.10 Gap Analysis for β-Naphthol Production

Gap refers to the space between "where we are" (the present state) and "where we want to be" (the target state). A gap analysis may also be referred to as a needs analysis, needs assessment or ***Need-Gap Analysis***.

The first step in conducting the so-called *Need-Gap Analysis* is to establish the specific target objectives by looking at the company's immediate and long term interest (mission statement, strategic goals and improvement objectives). The next step is to analyze current business processes by collecting relevant data on performance levels and how resources are presently allocated to these processes. This data can be collected from a variety of sources depending on what is being analysed. For example, by looking at documentation, conducting interviews with the experts and production managers, brainstorming and observing the production process. Lastly, after comparing the company's current state against the desirable and mandatory environmental as well as work-place safety requirements; a comprehensive plan can be developed. Such "plan" outlines the specific steps to take to fill the gap between its current and future states, and reach its target objectives.

Small and medium scale industries, in particular, can benefit from performing such *Need-Gap Analysis*. Such analysis could have the following THREE target objectives:

1. How to allocate resources?,
2. How to improve performance and profits? and
3. How to improve work-place safety and minimize environmental pollution loads?

In the following section, an effort has been made to present the improvements for short-term benefits as well as long-term benefits; based on the methodology described above.

Improvements for Short-Term Benefits

Significance of Temperature Control: Although the literature on the production process and efficiency improvement is limited, several Chinese patents (and a limited number of patents from other countries) are apparently available. However, owing to the issues associated with language barrier and cryptic details typically reported in patent documents, this literature did not prove to be useful in suggesting measures for improving the production process and efficiency of β-Naphthol production. In any case, we understand that there are several different steps, unit processes, and unit operations involved in the production of β-Naphthol. Some of these processes need to be operated over a very slim temperature range because the raw materials and intermediates involved in the unit process are temperature sensitive.

It is well understood that the kinetics of the steps involved in β-Naphthol production are rather complex and therefore, "manual control" of temperature proves to be inferior when compared with the so-called "automatic control". Inadequate temperature control causes the formation of unwanted isomers and side products – which eventually lead to wastage of raw materials or intermediates and, thus, lead to enhanced generation of wastewater and undesirable by-products. Needless to emphasise here that the overall yield of the desirable product, too, diminishes significantly in absence of sophisticated temperature control instrumentation – which further leads to a decrease in profits.

In view of the above kinetics-related issues, installation of the automatic temperature control instrumentation as well as sophisticated temperature measurement instrumentation are strongly recommended. Devising two separate instruments, one for automatic temperature control and one sophisticated temperature measurement is considered the best-practise for industrial chemical production. The redundancy and duplication in control and measurement instrumentation often proves to be a wise investment in the long run. Not only it improves the product yield and profits, but it also improves the process safety and decreases pollution.

Automation of Acid and / or Alkali Addition: By using a digital *p*H meter and linking it to the addition of acid / alkali in each unit process, stoichiometric addition of acid and / or alkali would be relatively easy. Thus, excessive addition of acid and / or alkali would be minimised and ultimately the quantity of salts dissolved in the reacting mass would decrease. These dissolved salts are carried forward to the treatment and recovery plant and finally end up in the mixed solid residue which is disposed of in CHW-TSDF. Through the closer control of *p*H in the respective reactors, especially in the Neutralization step, the β-Naphthol loss in the waste streams could also be minimised to a considerable extent.

The isomeric compounds and unwanted by-products are hindrances and effectively reduce the yield of β-Naphthol production. There could be the following three reasons for the formation of unwanted isomers; while synthesizing β-Naphthol:

a. Inherent limitations in the kinetics of various reaction stages which ultimately lead to the formation of isomers,

b. Improper control of reaction parameters like temperature, pressure, *etc.*, and

c. Excessive usage of acids and alkalis starting from sulphonation to final Neutralization step. Due to this, sodium salts (Na_2SO_3 and Na_2SO_4) get accumulated in the crude β-Naphthol slurry, further inhibiting the separation rate of β-Naphthol.

In view of the above thermodynamic and kinetics-related issues, installation of the sophisticated digital *p*H control instrumentation as well as an automated system for acid / alkali addition are strongly recommended. Devising two separate systems, one for sophisticated *p*H control and one for automated addition is considered the best-practise for industrial chemical production. The redundancy and duplication in these systems often proves to be a wise investment in the long run. Not only it improves the product yield and profits, but it also improves the process safety and decreases pollution.

Significance of Digital Flowmeters to Track Water Usage: As seen in the water budget, production of β-Naphthol is highly water-intensive. Keeping a track of water at every input and the output is essential from the point of view of having an accurate water balance and water budget. Currently, since there is no flow meter to keep track of the water usage, the values of the water usage are rough estimates. This is unacceptable. In order to have a perfect mass balance and water balance, every part of the water used in the plant needs to be tracked.

Therefore, the use of digital flowmeters at all the places in the plant where water is used is recommended. The planning and implementation of this recommendation should be expedited and taken up as the first priority.

Housekeeping and Maintenance: The investigation team from IIT Bombay visited this plant several times and discussed with persons from Production and Environment Protection teams. There was a great cooperation from these persons and the information was furnished efficiently through emails, completing the requested tabulated information, cooperating with the personnel from Vadodara Enviro Channel Limited (VECL) while collecting samples and obtaining data as well as through face-to-face interactions during the site visits. The IIT Bombay team is grateful to the company for the help and facilitation.

Frankly, whenever IIT Bombay team visited the production facility as well as ETP and STP, *prima facie* it appeared as though the overall upkeep and housekeeping was visibly poor. Most of the floors and surfaces inside the roof and columns of the shed were unclean, rusted and it was clear that the housekeeping related functions were generally given a low priority.

It is generally understood that the functions related to routine maintenance of equipment, reactors, piping, loading-unloading platforms, and staircases (ladders) become difficult and the overall surroundings have poor housekeeping. It is also understood that the frequency of maintenance, too, increases in the midst of unclean surroundings (more corrosion, frequent breakdown, difficulty in repairs and maintenance).

More importantly, the propensity for accidents, fire, explosion, injury at the workplace are generally found to enhance in the situations where overall maintenance and housekeeping is poor. The modern safety science, in fact, has been lately recommending for superlative interventions related to cleanliness, daily upkeep, and above all, the “preventive maintenance”.

Maintenance and calibration of all instrumentation and control hardware is of utmost importance, not only from the point of view of the production process and product purity but also from the point of view of minimization of pollution and enhancement of health and safety of the workers. Poorly or rarely calibrated instrumentation and control hardware will often lead to addition of an incorrect amount of inputs to the reactor or give a false picture of the conditions in the reactor. This might, in turn, impact the indoor air quality, safety of the workers, and generation of pollution from the production plant. If the production plant is not properly maintained, the probability of malfunctioning of the instrumentation and process control devices would increase. Also, the functioning of ETP and STP will get affected beyond the certain extent of negligence in the production plant.

In sum, it is well-known that the β-Naphthol production process is extremely complicated and rather highly polluting. No wonder, several states in India and several countries in the world have imposed a ban on the production of these dye-intermediates. Because the raw materials and intermediates involved in the production of β-Naphthol are extremely reactive and corrosive; the maintenance routine should be commensurate with the propensity of rusting and evolution of fumes in the process plant.

Clearly, poor maintenance and upkeep could generate an unsafe work environment and pose higher risk to the workers' safety and environment. In addition to this, safety devices such as relief valves, process control equipment, pressure relief valves, etc. must be maintained and replaced as per the industry standards and the best-recommended practices.

The investigation team from IIT Bombay has taken a serious note of these facts and would recommend rather strongly that the housekeeping and maintenance should be improved remarkably in the nearest future. Adequate Personal Protective Equipment (PPE), uniform for all personnel, labelling of equipment, tanks and pipelines should be taken up as the first priority and serious efforts should be made to create the positive first impression.

Constructing a New and Robust Stormwater Collection and Treatment System: The investigation team from IIT Bombay visited Bodal Unit VII multiple times and has taken note of the fact that the stormwater collection system is inadequate in its current installation. Bodal Unit VII produces H-Acid, Vinyl Sulphone, β-Naphthol and crude dyestuff. It is a well-known fact that although the H-Acid final product is a greyish-white powder, H-Acid solutions in water have a dark blue to blackish colour even at low concentrations. This property of H-Acid is the primary reason that the stormwater runoff from the H-Acid plant and its surrounding areas will more often than not have a dark blue or blackish colour and some amount of COD.

A new stormwater drainage system should be constructed which will adequately intercept the surface water and stormwater runoff as per industry standards and divert the water to the ETP for treatment. Since the stormwater from this industry will have COD contributed by highly recalcitrant organic compounds, under no condition should the surface water runoff and/or stormwater runoff be let off into the channel or the environment without treatment in the ETP first. Hence, a new and robust stormwater collection and treatment system must be constructed to intercept and treat the stormwater and surface water runoff as per industry standards. This endeavour must be taken up as the first priority.

Recovery of β-Naphthol from the Cake-washing Wastwater: It is well known that the wastewater stream from cake-washing after the Quenching step carries some amount of β-Naphthol sodium salt and cake-washing of the crude β-Naphthol carries some amount of dissolved β-Naphthol, which is essentially the product loss. Thus, there is a decrease in the efficiency and yield of the product.

The presence of these compounds in the wastewater contributes to COD and causes problems during the treatment or, especially, during the reuse of the said wastewater. Reportedly, at Bodal Unit VII, all the cake-washing wastewater is reused back into the process in various stages. Hence, apart from the product loss and decrease in efficiency, the presence of these compounds (along with other organic molecules) in the wastewater will be a hindrance during the reuse of this wastewater.

Apparently, as per a few Chinese patents, it is possible to recover the β-Naphthol sodium salt and β-Naphthol by using Solvent Extraction followed by concentration to separate out salts and finally Distillation to recover much purer water which is much more feasible to reuse in the β-Naphthol production process.

The targeted R&D, therefore, will need to be conducted to evaluate the applicability of this technology in the β-Naphthol production process, as well as cover the costs of purchasing the patent.

Construction of Dedicated Shed for Temporary Storage of Fly Ash and Sludge Before Disposal: The investigation team from IIT Bombay has noticed that the storage areas of fly ash, Gypsum Sludge, and Iron Sludge in Bodal Unit VII need to be renovated. The current 'storage yards' are distributed at many places on the campus of the industry and it might be useful to renovate aimed at modernization of all storage areas.

The storage area of fly ash and sludges must be covered and must have a concrete base surrounded by a leak-proof dike to collect the oozing water and any leachate. The dike should be devised with pumping facility to transfer the liquid collected in the dike to ETP for further treatment before disposal in the VECL channel. This effort must be taken up as the first priority.

Improvements for Long-Term Benefits

Following are the suggestions for interventions that could potentially yield the so-called "long-term benefits":

Alternate Production Routes for Cleaner Production: The current method of β-Naphthol production is through the Naphthtlene sulphonation route. From the facts and details as presented in the above sections, it is clear that while this production route gives an impeccable yield of β-Naphthol, it also leads to a high and especially recalcitrant environmental pollution load. In addition, other problems related to the current production route are difficulty in removal of by-products, manufacturing costs, scale of mass production, and dependency on manual labour.

Hence, it is of utmost importance to look into alternatives – alternate production routes with different raw materials and certain process modifications – which will lead to a Cleaner Production of β-Naphthol.

Reportedly, according to various patents (American and Chinese) and commercially available processes, alternate production routes for β-Naphthol are currently practised in the world. However, targeted R&D efforts are required to implement them in the existing production process used by Bodal Unit VII. In other words, those innovations will have to be perfected to reach the desired yield of β-Naphthol, as in the Naphthalene sulphonation-based process.

The most viable alternative currently is the 'Alkylnaphthalene hydroperoxide' route – which is briefly described below:

1. The first step is a preparation of (say) isopropylnaphthalene from two starting materials, naphthalene and propylene.
2. The second step is the oxidation of the isopropylnaphthalene thus obtained to isopropylnaphthalene hydroperoxide with an Oxidizing agent in the presence of an alkali.
3. The last step is a cleavage of the hydroperoxide thus obtained into β-Naphthol and acetone in the presence of an acid catalyst such as Sulphuric Acid.

4. It is true that by-products are generated in this process as well and the generation of α-Naphthol is inevitable. But through recrystallization using a solvent, pure β-Naphthol can be separated. The separation efficiency is higher than the conventional distillation method since the boiling points of some of the by-products are too close together. In addition to a purer product, the water usage is severly reduced. The performance of this process depends on the selection of the organic solvent. Hence, R&D is required for determination of the best possible alternative of organic solvent.

The targeted R&D, therefore, will need to be conducted to evaluate the relative benefits of the alternate processes using different raw materials and the subsequent reduction of the environmental load as well as cover the costs of purchasing the patent.

1.11 Brief Manufacturing Process of Crude Synthetic Dyes

The brief manufacturing process, the stoichiometry and gap analysis of H-Acid, Vinyl Sulphone and β-Naphthol production plants were presented in sections 1.2 through 1.10 The brief manufacturing process of Crude Synthetic Dyes is presented in this section. Currently, at Bodal Unit VII, three Crude Synthetic Dyes are produced. The first one being Reactive Black-5 (RB-5), the second one being Reactive Red-195 (RR-195) and the third one being Acid Black-210 (AB-210).

Brief Manufacturing Process of Reactive Black-5:

The brief production process flow diagram of Reactive Black-5 is given in **Figure 1.9**. The major production process details are given below:

1. Diazotization
    1. Diazotization of Vinyl Sulphone is carried out in this step using a solution of Vinyl Sulphone in water with Hydrochloric Acid and Sodium Nitrite at 50ºC.
    2. Ice is added to control the temperature and maintain a cool environment since the reaction is exothermic.

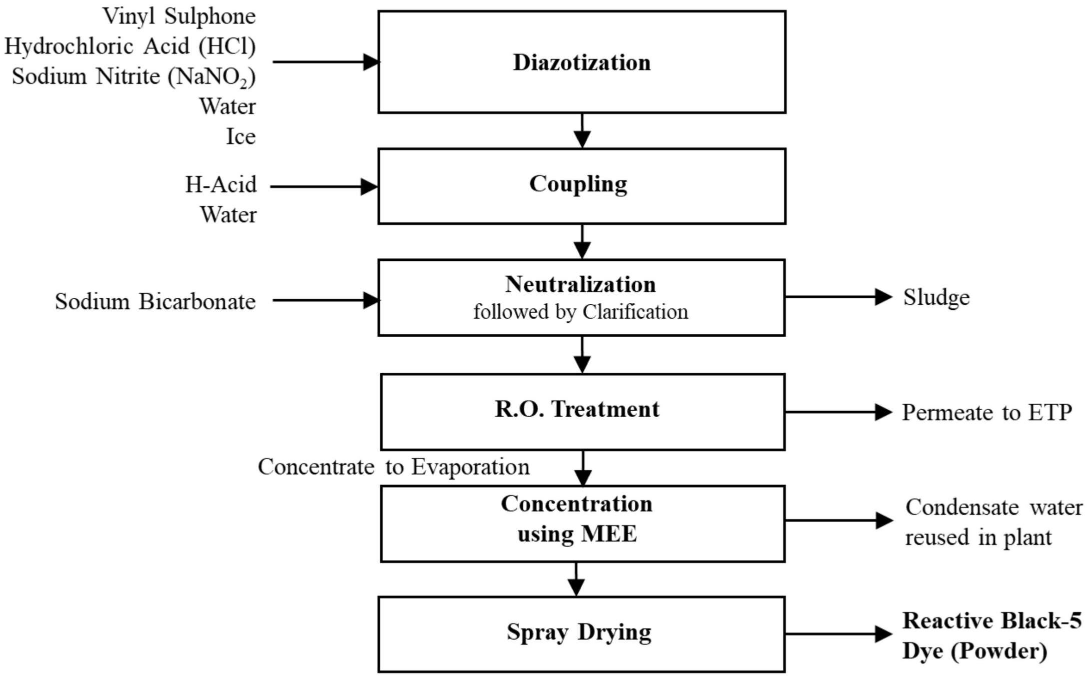


Figure 1.9 The production process flow diagram for Reactive Black-5, as practised in the batch-wise production, at Bodal Unit VII

   c. The reaction leads to the formation of the Diazonium chloride salt of Vinyl Sulphone.
   d. The reaction mass is then taken to the Coupling step vessel.

3. Coupling
   a. H-Acid solution is prepared in water.
   b. This H-Acid solution is then added to the Diazotized reaction mass received from the previous reactor.
   c. The reaction mass is now stirred for 12 hours.
   d. Thus, H-Acid is coupled with the diazotized mass and HCl is formed as the by-product of the reaction.

4. Neutralization
   a. The HCl generated in the reaction needs to be neutralized.
   b. Sodium Bicarbonate is added to neutralize the HCl. Thus, Sodium Chloride (NaCl) is formed.
   c. The neutralized mass is now Clarified to separate out any remaining solid material such as unreacted reactants, some mixed by-products, *etc.*
   d. The clarified mass is then sent to the R.O. Treatment Unit.

5. R.O. Treatment
   a. The R.O. Treatment is performed in order to separate the heavy dye salt from the other mixed lighter weight salts.
   b. The permeate from the R.O. unit is sent to the ETP for treatment and disposal.
   c. The concentrate from the R.O. unit is sent to the MEE for further concentration by removal of water.

5. Concentration and Spray Drying

    a. The concentrate from the R.O. Treatment unit, now containing almost exclusively the dye salt, is subjected to concentration using Multiple Effect Evaporation (MEE).

    b. The condensate water obtained from the top of the MEE is reused in the plant.

    c. The bottoms, or concentrate, from the MEE is then subjected to Spray Drying to remove the remaining water and thus, the final Reactive Black-5 dye powder is obtained.

Brief Manufacturing Process of Reactive Red-195:

The brief production process flow diagram of Reactive Red-195 is given in **Figure 1.10**. The major production process details are given below:

1. Cyanurization

    a. Diazotization of Vinyl Sulphone is carried out in this step using a solution of Vinyl Sulphone in water with Hydrochloric Acid and Sodium Nitrite at 50ºC.

    b. Ice is added to control the temperature and maintain a cool environment since the reaction is exothermic.

    c. The reaction leads to the formation of the Diazonium chloride salt of Vinyl Sulphone. Further, Cyanuric Chloride is added to the reaction vessel.

    d. Thus, ‘cyanurized mass of Vinyl Sulphone’ is obtained.

    e. The reaction mass is then taken to the 1st Coupling vessel.

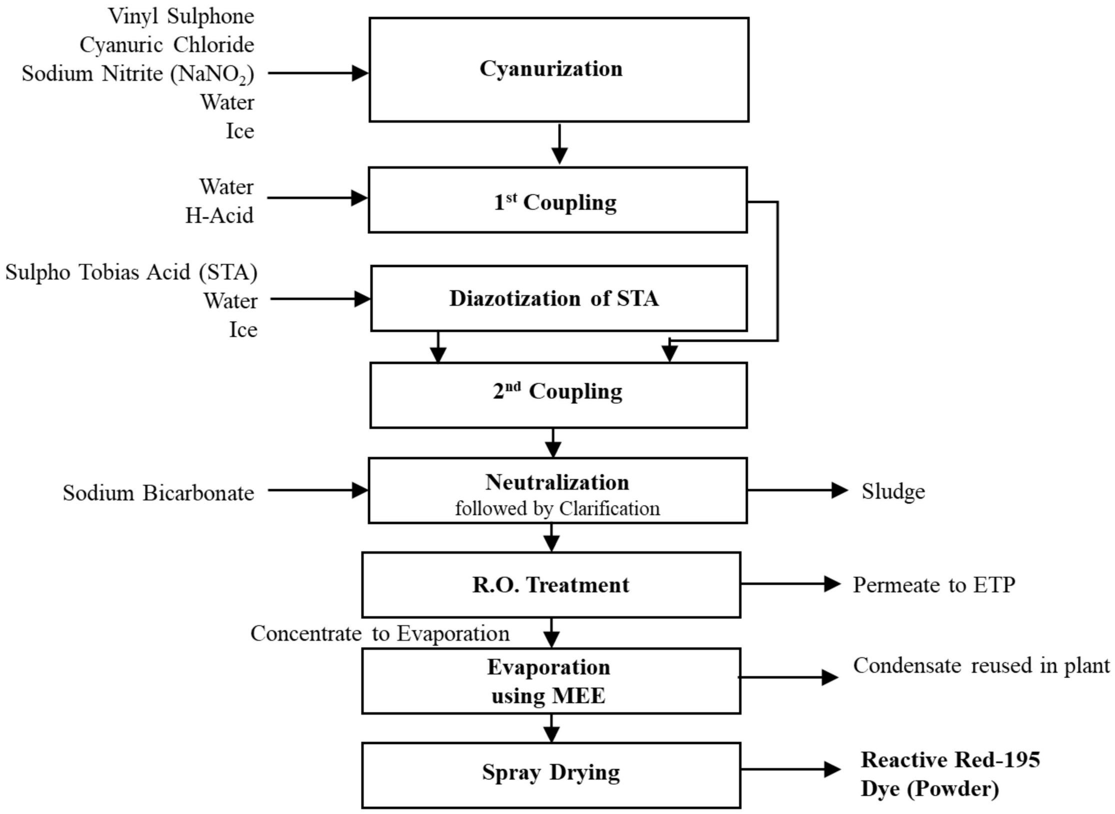


Figure 1.10 The production process flow diagram for Reactive Red-195, as practised in the batch-wise production, at Bodal Unit VII

3. 1st Coupling
    a. H-Acid solution is prepared in water.
    b. This H-Acid solution is then added to the ‘cyanurized mass of Vinyl Sulphone’ received from the previous reactor.
    c. The temperature is maintained at 55ºC.
    d. Thus, H-Acid is coupled with the ‘cyanurized mass of Vinyl Sulphone’ and HCl is formed as the by-product of the reaction.
4. Diazotization of STA
    a. Diazotization of Sulpho Tobias Acid (STA) is carried out in this step using a solution of STA in water with Hydrochloric Acid and Sodium Nitrite at 50ºC.
    b. Ice is added to control the temperature and maintain a cool environment since the reaction is exothermic.
    c. The reaction mass is then taken to the 2nd Coupling vessel.
5. 2nd Coupling
    a. The Diazotized mass of STA and the reaction mass from 1st Coupling step are coupled in this step.
    b. The temperature is maintained using Ice since the reaction is exothermic.
    c. The reaction mass is now stirred for 12 hours.
    d. Thus, the Reactive Red-195 dye molecule is synthesized.
    e. HCl is formed as the by-product of the reaction.

    5. Neutralization

    a. The HCl generated in the reaction needs to be neutralized.
    b. Sodium Bicarbonate is added to neutralize the HCl. Thus, Sodium Chloride (NaCl) is formed.

   c. The neutralized mass is now Clarified to separate out any remaining solid material such as unreacted reactants, some mixed by-products, *etc.*

   d. The clarified mass is then sent to the R.O. Treatment Unit.

6. R.O. Treatment

   d. The R.O. Treatment is performed in order to separate the heavy dye salt from the other mixed lighter weight salts.

   e. The permeate from the R.O. unit is sent to the ETP for treatment and disposal.

   f. The concentrate from the R.O. unit is sent to the MEE for further concentration by removal of water.

7. Concentration and Spray Drying

   g. The concentrate from the R.O. Treatment unit, now containing almost exclusively the dye salt, is subjected to concentration using Multiple Effect Evaporation (MEE).

   h. The condensate water obtained from the top of the MEE is reused in the plant.

   i. The bottoms, or concentrate, from the MEE is then subjected to Spray Drying to remove the remaining water and thus, the final Reactive Red-195 dye powder is obtained.

Brief Manufacturing Process of Acid Black-210:

The brief production process flow diagram of Acid Black-210 is given in **Figure 1.11**. The major production process details are given below:

1. Diazotization of PNA

   a. Diazotization of p-Nitro Aniline (PNA) is carried out in this step using a solution of PNA in water with Hydrochloric Acid and Sodium Nitrite at 60ºC and stirred for 15 minutes.

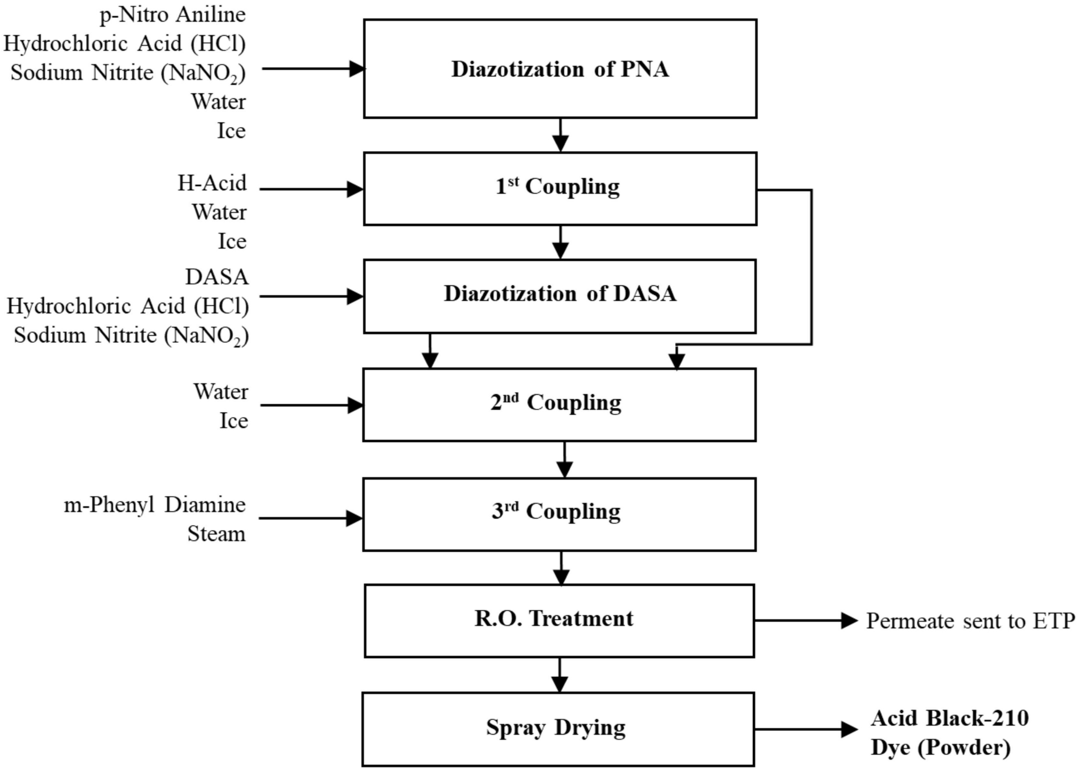


Figure 1.11 The production process flow diagram for Acid Black-210, as practised in the batch-wise production, at Bodal Unit VII

b. Ice is added to control the temperature and maintain a cool environment since the reaction is exothermic. The temperature is maintained between 0-5ºC for a period of 2 hours.

c. The excess Sodium Nitrite is removed by reaction with Sulphamic Acid.

d. The reaction leads to the formation of the Diazonium chloride salt of PNA.

e. The reaction mass is then taken to the 1st Coupling vessel.

3. 1st Coupling
    a. H-Acid solution is prepared in water.
    b. This H-Acid solution is then added to the Diazonium chloride salt of PNA received from the previous reactor.
    c. The temperature is maintained between 5-10ºC.
    d. Soda Ash is added to bring the pH between 6.5 and 7. Stir the reaction mass for 12 hours.
    e. Thus, H-Acid is coupled with the Diazonium chloride salt of PNA and HCl is formed as the by-product of the reaction.

3. Diazotization of DASA

    a. Diazotization of DASA is carried out in this step using a solution of DASA in water with Hydrochloric Acid and Sodium Nitrite at 5ºC.

    b. Ice is added to control the temperature and maintain a cool environment since the reaction is exothermic.

    c. The reaction mass is then taken to the 2nd Coupling vessel.

4. 2nd Coupling
    a. The Diazotized mass of DASA and the reaction mass from 1st Coupling step are coupled in this step.
    b. The temperature is maintained at 5ºC using Ice since the reaction is exothermic.

   c. The reaction mass is now stirred for 2 hours.
   d. HCl is formed as the by-product of the reaction.
   e. The pH is maintained at 8.5 by addition of Soda Ash.

5. 3rd Coupling
   a. m-Phenyl Diamine (MPD) and the reaction mass from 2nd Coupling step are coupled in this step.
   b. The temperature is maintained at 70ºC using steam.
   c. The reaction mass is now stirred for 12 hours.
   d. The pH is maintained at 8.5.
   e. Thus, Acid Black-210 dye molecule is synthesized. The reaction mass is then sent to the R.O. Treatment unit for removal of the by-products and other dissolved salts.

6. R.O. Treatment
   a. The R.O. Treatment is performed in order to separate the heavy dye salt from the other mixed lighter weight salts.
   b. The permeate from the R.O. unit is reused in the plant for washing.
   c. The concentrate from the R.O. unit is sent to the Spray for further concentration by removal of water.

7. Spray Drying
   a. The concentrate from the R.O. Treatment unit, now containing almost exclusively the dye salt, is subjected to Spray Drying to remove the excess water.
   b. Thus, the final Acid Black-210 dye powder is obtained.

1.12 Stoichiometry and Mass Balance for Crude Synthetic Dyes Production

As discussed earlier in Section 1.11, Figure 1.9, Figure 1.10 and Figure 1.11 illustrate the production process flow diagrams for the Crude Synthetic Dyes (*namely*; Reactive Black-5, Reactive Red-195, and Acid Black-210), as practised in the batch-wise production, at Bodal Unit VII. At the outset, all the important reactions performed in the production process of the Crude Synthetic Dyes are briefly presented below:

In this section, the stoichiometry and mass balance for Crude Synthetic Dyes production is split in three parts. The first one being for production of Reactive Black-5, the second one being for the production of Reactive Red-195, and the third one for the production of Acid Black-210.

The Basis and Assumptions Used for Mass Balances:

It must be noted here that the exact composition of Reactive Black-5, Reactive Red-195, and Acid Black-210 (product assay) was not made available to the IITB team by Bodal Unit VII. However, it was reported to IITB that the maximum permissible impurities cannot exceed 5% w/w in the final product (sum of salts and unreacted intermediates). In any case, it is well known that the manufacturers always aim for overseas markets and try to keep the impurities as low as possible because the presence of the impurities (especially the salts) interferes with the uptake rates of dyes during dyeing operations.

Hence, all the calculations pertaining to dyes assume that the R.O. membranes would block passage of all the dye molecules as well as all the unreacted entities during the membrane separation in dye manufacturing plants. Consequently, 99.5% mass of dye as well as 100% mass of the unreacted entities will get transferred to the concentrated stream – which would be subsequently subjected to Spray Drying operation. However, no salt would be transferred to the concentrated stream because it is well known that the dissolved salts are extremely small molecules / ion when compared with the dye and unreacted entities. As a result, it is envisaged that Bodal Unit VII manufactures dyes with 1 to 3% w/w impurity in the final product (after Spray Drying) emerging from the unreacted intermediates in the final product. Further, 100% of salts are transferred to permeates through the operation of R.O. units in the respective dye manufacturing units. The TDS imparted to the R.O.

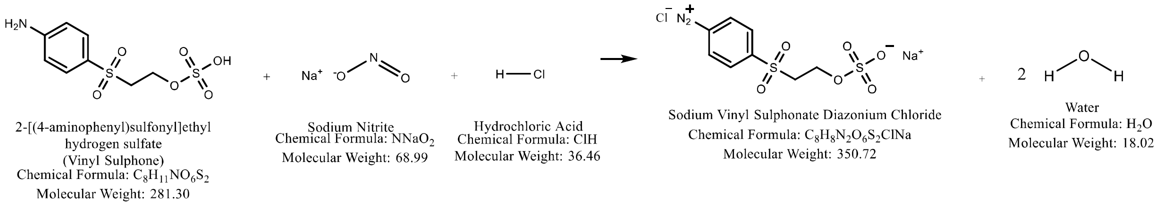
permeate streams sent to ETP are estimated based on the above asumptions (refer to Table 1.17).

Unfortunately, Bodal Unit VII did not share the quantities of the three dyes (Reactive Black-5, Reactive Red-195, and Acid Black-210) manufactured during 2018-19, 2017-18 and 2016-17. Instead, the data on the total quantities of dyes manufactured in the respective years were provided to IITB team.

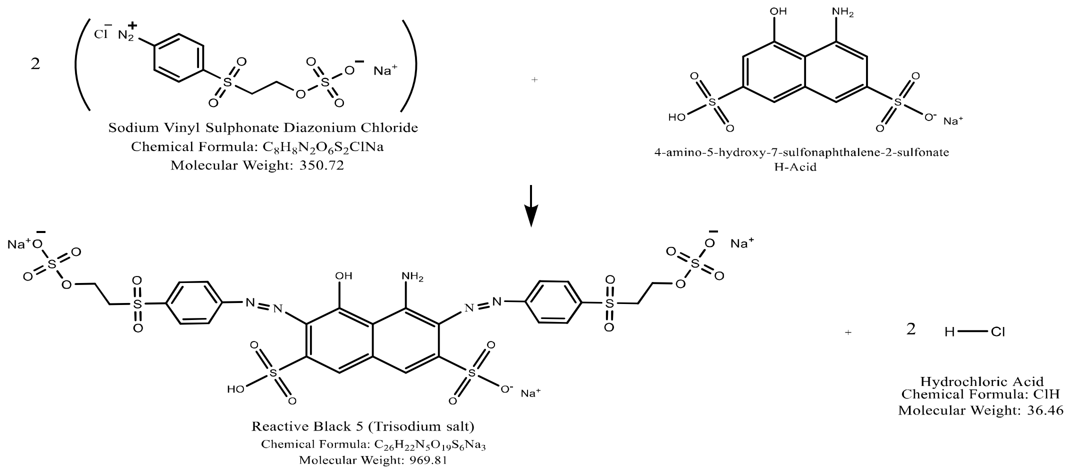
As a result, the author of this report could not accurately estimate the pollutant loads sent to ETP on account of production of the three dyes. Out of helplessness, the author has assumed that the quantities of the three dyes were equal every year and the estimates were performed. This assumption has introduced an undesirable inaccuracy in the mass balances and estimates presented in this report. The author of this report cannot hide his astonishment. It is difficult to understand why the production data should be treated as the "confidential information"!

Stoichiometry and Mass Balance for Reactive Black-5:

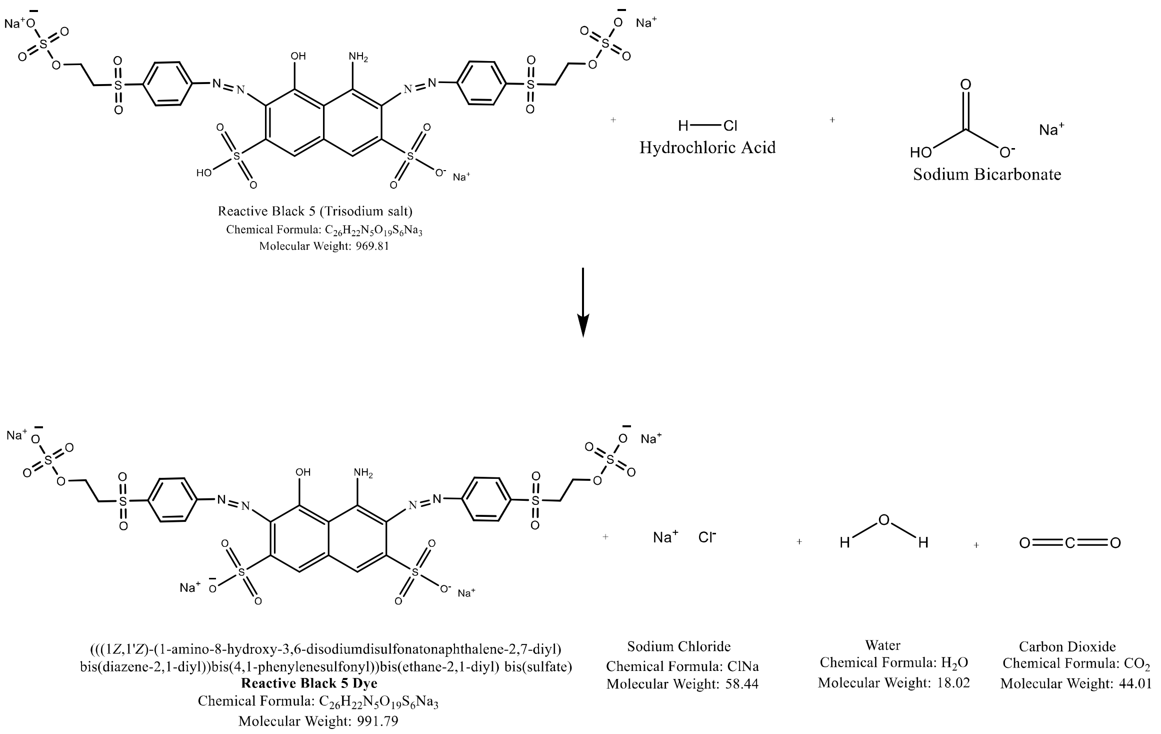
1. Diazotization of Vinyl Sulphone



2. 1st Coupling



3. Neutralization

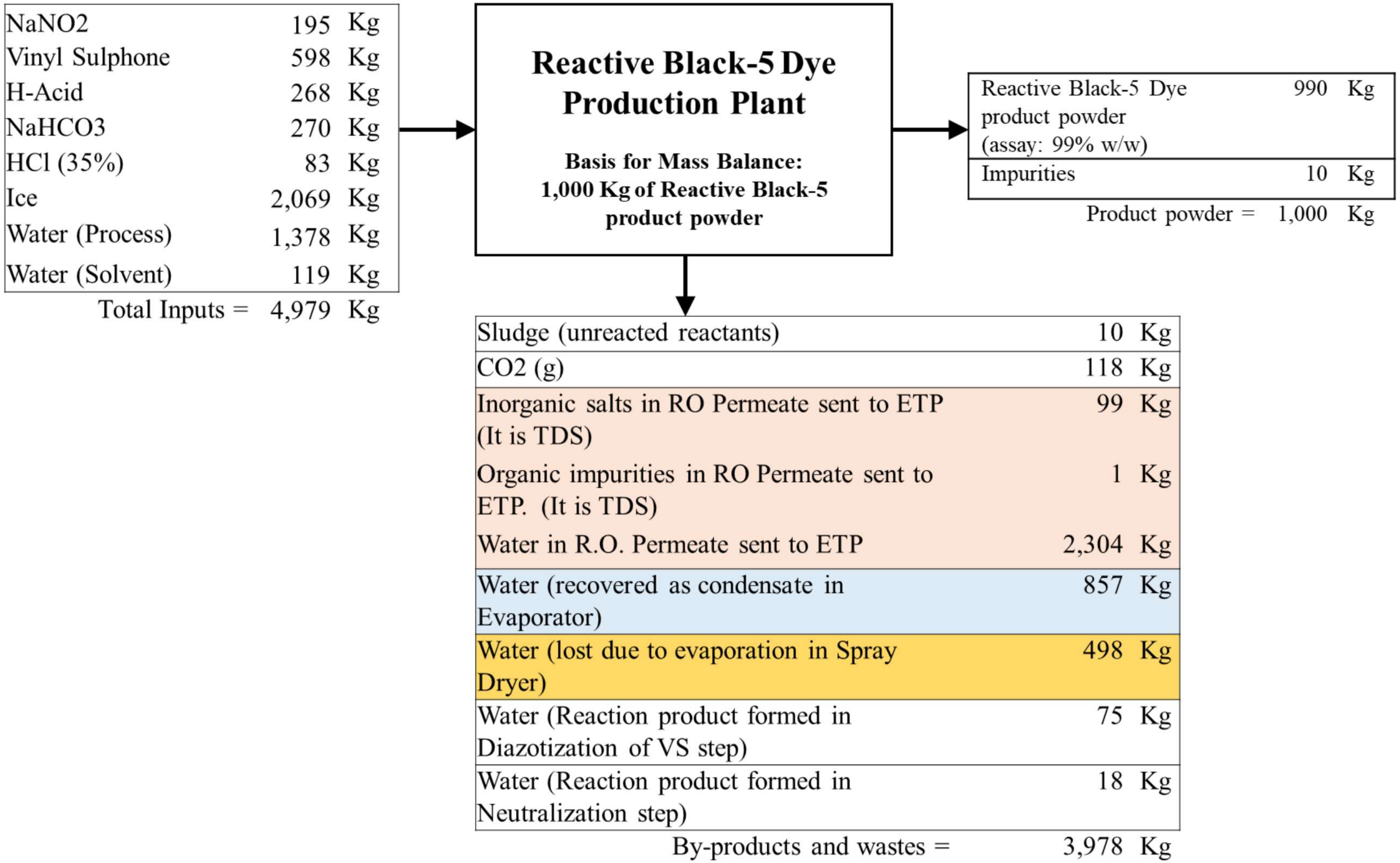


With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant "as a production unit" is presented in **Figure 1.12**; with the basis of 1 Ton production of RB-5 at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of RB-5 synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing RB-5 molecule is elaborated in this analysis. **Table 1.11** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of RB-5 at Bodal Unit VII. As presented in the Table, 1 Ton of RB-5 production also produces 93 Kg of Water (as by-product). This water, however, remains mixed with the bulk of the reacting mass in the reactor and eventually gets removed downstream through one or more unit operations.

Critical Discussion on the Water Budget: Further, **Table 1.12** depicts the detailed 'Water Budget' for production of one Ton of RB-5 at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the RB-5 production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 3.659 Ton per Ton of RB-5 production. More importantly, Table 1.12 also elaborates on all the efforts of reuse and recycle of the recovered water within the process plant. Because of these efforts, a substantial quantity of water is being saved and reused (0.857 Ton of water per Ton of RB-5 production). Thus, nearly 25% water is being recycled.

In summary, the net freshwater requirement works out to be 2.802 Ton of water per Ton of RB-5 production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of effluent sent to ETP, moisture associated with product as well as on account of evaporation losses (see Table 1.12).



NaNO2	195	Kg
Vinyl Sulphone	598	Kg
H-Acid	268	Kg
NaHCO3	270	Kg
HCl (35%)	83	Kg
Ice	2,069	Kg
Water (Process)	1,378	Kg
Water (Solvent)	119	Kg
Total Inputs =	4,979	Kg

Reactive Black-5 Dye product powder (assay: 99% w/w)	990	Kg
Impurities	10	Kg
Product powder =	1,000	Kg

Sludge (unreacted reactants)	10	Kg
CO2 (g)	118	Kg
Inorganic salts in RO Permeate sent to ETP (It is TDS)	99	Kg
Organic impurities in RO Permeate sent to ETP. (It is TDS)	1	Kg
Water in R.O. Permeate sent to ETP	2,304	Kg
Water (recovered as condensate in Evaporator)	857	Kg
Water (lost due to evaporation in Spray Dryer)	498	Kg
Water (Reaction product formed in Diazotization of VS step)	75	Kg
Water (Reaction product formed in Neutralization step)	18	Kg
By-products and wastes =	3,978	Kg

Figure 1.12 Input-output analysis of Reactive Black-5 dye (RB-5) at Bodal Unit VII (Basis: 1,000 Kg of RB-5 product powder)

Table 1.11 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of Reactive Black-5 at Bodal Unit VII

Role of Water in the Process Plant	**Quantity per Ton of RB-5 production (Kg)**
Water (Reaction Product) formed in Diazotization of VS step	-75
Water (Reaction Product) formed in Neutralization step	-18
Net Water Consumption (in reactive steps) =	**-93** *

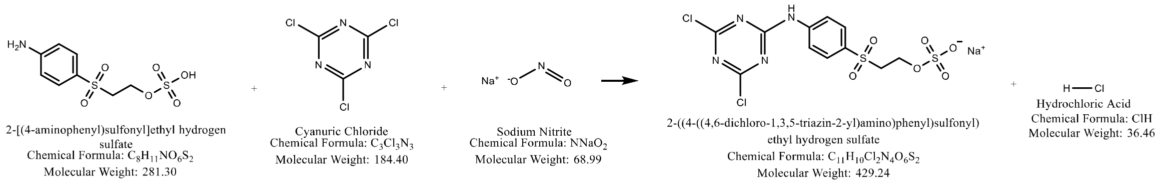
*93 Kg of water is generated during production of one Ton of RB-5.

Table 1.12 A detailed 'Water Budget' for production of one Ton of Reactive Black-5 at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the RB-5 production plant.

Role of Water in the Process Plant	**Quantity per Ton of RB-5 production (Kg)**
Input of Water (Basis: 1 Ton of RB-5)	
Water (Solvent)	119
Water (Process – used in multiple unit processes)	1,378
Water (for production of Ice)	2,069
Water (generated in multiple reactive steps)	93
Total input of water for one Ton of RB-5 =	**3,659**
Emission of Water (Basis: 1 Ton of RB-5)	
Water (in form of condensate after Evaporation) (This will be used in the next batch.)	-857
Reused and recycled water (condensate after Evaporation from previous batch)	857
Water in R.O. permeate (sent to ETP)	-2,304
Water lost in Spray Drying	-498
Total input of water for one Ton of RB-5 =	**-3,659**
Condensate Water reused from various sources	**857**
Water leaving the system (associated with solids & evaporation loss)	**-2,802**
Net freshwater requirement (3,659– 857 = 1,793)	**2,802**

Stoichiometry and Mass Balance for Reactive Red-195:

1. Diazotization and Cyanurization of Vinyl Sulphone



2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate
Chemical Formula: $C_8H_{11}NO_6S_2$
Molecular Weight: 281.30

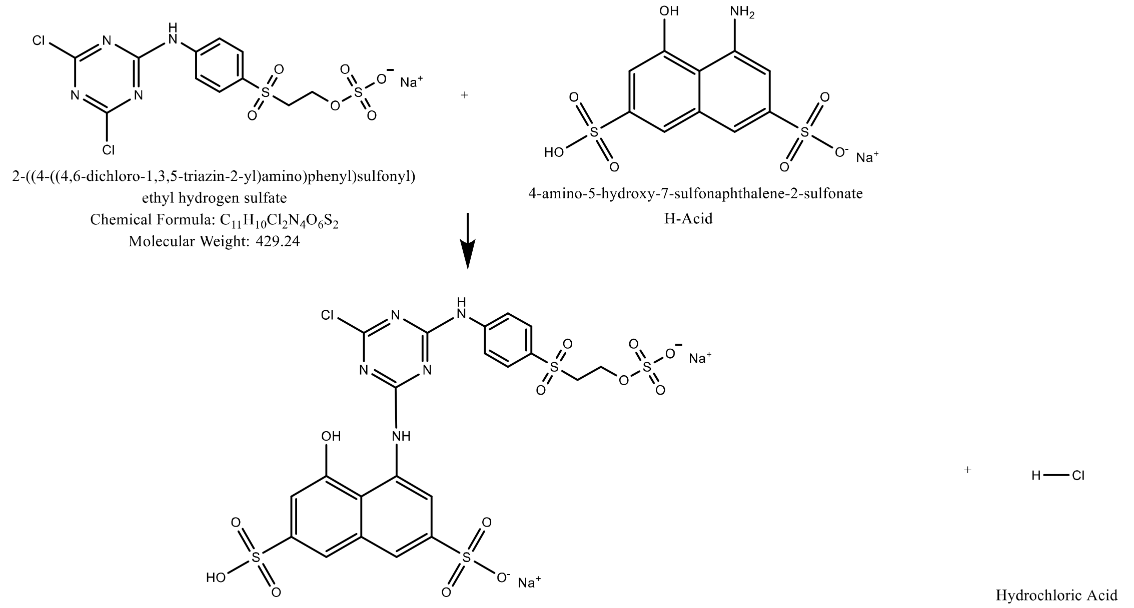
Cyanuric Chloride
Chemical Formula: $C_3Cl_3N_3$
Molecular Weight: 184.40

Sodium Nitrite
Chemical Formula: $NNaO_2$
Molecular Weight: 68.99

2-((4-((4,6-dichloro-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl) ethyl hydrogen sulfate
Chemical Formula: $C_{11}H_{10}Cl_2N_4O_6S_2$
Molecular Weight: 429.24

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36.46

2. 1st Coupling



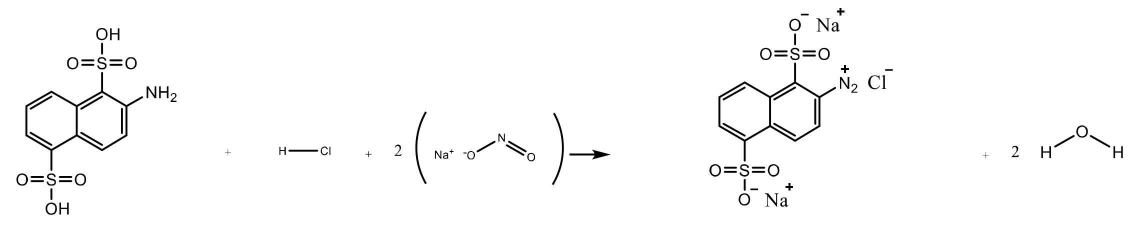
2-((4-((4,6-dichloro-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl) ethyl hydrogen sulfate
Chemical Formula: $C_{11}H_{10}Cl_2N_4O_6S_2$
Molecular Weight: 429.24

4-amino-5-hydroxy-7-sulfonaphthalene-2-sulfonate
H-Acid

2-((4-((4-chloro-6-((8-hydroxy-6-sulfo-3-sulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl)ethyl disodium sulfate
Chemical Formula: $C_{21}H_{16}ClN_5O_{13}S_4Na_2$
Molecular Weight: 756.05

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36.46

3. Diazotization of STA



2-aminonaphthalene-1,5-disulfonic acid
Sulpho Tobias Acid (STA)
Chemical Formula: $C_{10}H_9NO_6S_2$
Molecular Weight: 303.30

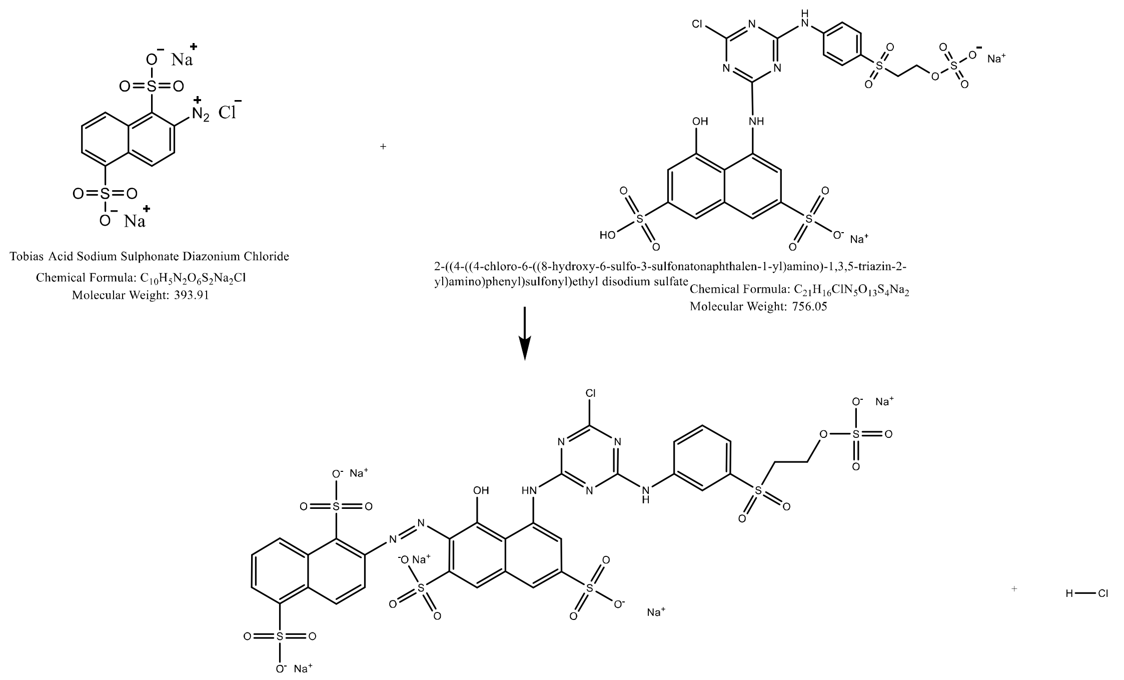
Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36.46

Sodium Nitrite
Chemical Formula: $NNaO_2$
Molecular Weight: 68.99

Tobias Acid Sodium Sulphonate Diazonium Chloride
Chemical Formula: $C_{10}H_5N_2O_6S_2Na_2Cl$
Molecular Weight: 393.91

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

4. 2nd Coupling



Tobias Acid Sodium Sulphonate Diazonium Chloride
Chemical Formula: $C_{10}H_5N_2O_6S_2Na_2Cl$
Molecular Weight: 393.91

2-((4-((4-chloro-6-((8-hydroxy-6-sulfo-3-sulfonatonaphthalen-1-yl)amino)-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl)ethyl disodium sulfate
Chemical Formula: $C_{21}H_{16}ClN_5O_{13}S_4Na_2$
Molecular Weight: 756.05

2-((3-((4-chloro-6-((7-((1,5-disulfonatonaphthalen-2-yl)diazenyl)-8-hydroxy-3,6-disulfonatonaphthalen-1-yl) amino)-1,3,5-triazin-2-yl)amino)phenyl)sulfonyl)ethyl sulfate
Reactive Red-195
Chemical Formula: $C_{31}H_{19}ClN_7O_{19}S_6Na_5$
Molecular Weight: 1134.82

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36.46

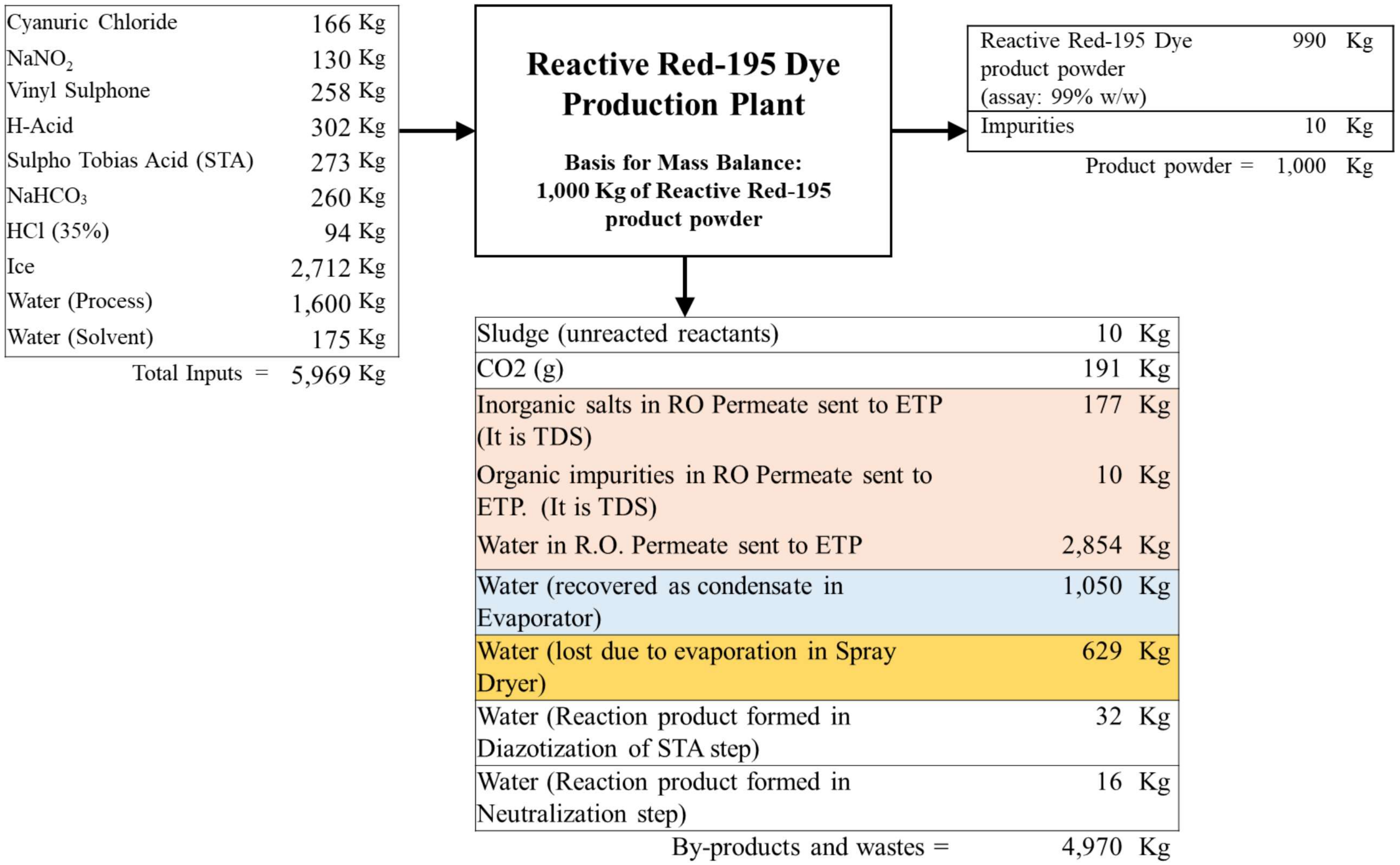
With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant "as a production unit" is presented in **Figure 1.13**; with the basis of 1 Ton production of RR-195 at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of RR-195 synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing RR-195 molecule is elaborated in this analysis. **Table 1.13** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of RR-195 at Bodal Unit VII. As presented in the Table, 1 Ton of

RR-195 production also produces 47 Kg of Water (as by-product). This water, however, remains mixed with the bulk of the reacting mass in the reactor and eventually gets removed downstream through one or more unit operations.

Critical Discussion on the Water Budget: Further, **Table 1.14** depicts the detailed 'Water Budget' for production of one Ton of RR-195 at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the RR-195 production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 4.354 Ton per Ton of RR-195 production. More importantly, Table 1.14 also elaborates on all the efforts of reuse and recycle of the recovered water within the process plant. Because of these efforts, a substantial quantity of water is being saved and reused (1.05 Ton of water per Ton of RR-195 production). Thus, nearly 25% water is being recycled.

In summary, the net freshwater requirement works out to be 3.484 Ton of water per Ton of RR-195 production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of effluent sent to ETP, moisture associated with product as well as on account of evaporation losses (see Table 1.14).



Cyanuric Chloride	166 Kg
$NaNO_2$	130 Kg
Vinyl Sulphone	258 Kg
H-Acid	302 Kg
Sulpho Tobias Acid (STA)	273 Kg
$NaHCO_3$	260 Kg
HCl (35%)	94 Kg
Ice	2,712 Kg
Water (Process)	1,600 Kg
Water (Solvent)	175 Kg
Total Inputs =	5,969 Kg

Reactive Red-195 Dye Production Plant

Basis for Mass Balance:
1,000 Kg of Reactive Red-195 product powder

Reactive Red-195 Dye product powder (assay: 99% w/w)	990 Kg
Impurities	10 Kg
Product powder =	1,000 Kg

Sludge (unreacted reactants)	10 Kg
CO2 (g)	191 Kg
Inorganic salts in RO Permeate sent to ETP (It is TDS)	177 Kg
Organic impurities in RO Permeate sent to ETP. (It is TDS)	10 Kg
Water in R.O. Permeate sent to ETP	2,854 Kg
Water (recovered as condensate in Evaporator)	1,050 Kg
Water (lost due to evaporation in Spray Dryer)	629 Kg
Water (Reaction product formed in Diazotization of STA step)	32 Kg
Water (Reaction product formed in Neutralization step)	16 Kg
By-products and wastes =	4,970 Kg

Figure 1.13 Input-output analysis of Reactive Red-195 dye (RR-195) at Bodal Unit VII (Basis: 1,000 Kg of RR-195 product powder)

Table 1.13 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of Reactive Red-195 at Bodal Unit VII

Role of Water in the Process Plant	**Quantity per Ton of RR-195 production (Kg)**
Water (Reaction Product) formed in Diazotization of STA step	-32
Water (Reaction Product) formed in Neutralization step	-16
Net Water Consumption (in reactive steps) =	**-47 ***

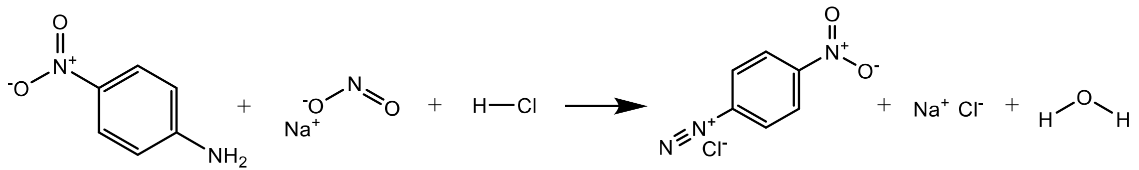
*47 Kg of water is generated during production of one Ton of RR-195.

Table 1.14 A detailed ‘Water Budget’ for production of one Ton of Reactive Red-195 at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the RR-195 production plant.

Role of Water in the Process Plant	**Quantity per Ton of RR-195 production (Kg)**
Input of Water (Basis: 1 Ton of RR-195)	
Water (Solvent)	175
Water (Process – used in multiple unit processes)	1,600
Water (for production of Ice)	2,712
Water (generated in multiple reactive steps)	47
Total input of water for one Ton of RR-195 =	**4,354**
Emission of Water (Basis: 1 Ton of RR-195)	
Water (in form of condensate after Evaporation) (This will be used in the next batch.)	-1,050
Reused and recycled water (condensate after Evaporation from previous batch)	1,050
Water from R.O. step (sent to ETP)	-2,854
Water lost in Spray Drying	-629
Total input of water for one Ton of RR-195 =	**-4,354**
Condensate Water reused from various sources	**1,050**
Water leaving the system (associated with solids & evaporation loss)	**-3,484**
Net freshwater requirement (4,354– 1,050 = 3,484)	**3,484**

Stoichiometry and Mass Balance for Acid Black-210:

1. Diazotization PNA



para-nitroaniline
Chemical Formula: $C_6H_6N_2O_2$
Molecular Weight: 138.13

Sodium Nitrite
Chemical Formula: $NNaO_2$
Molecular Weight: 68.99

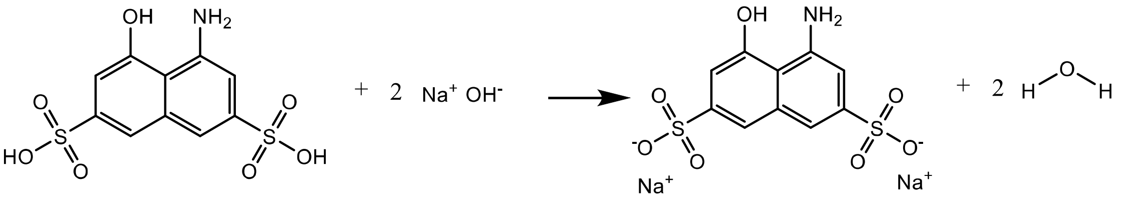
Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36.46

para-nitrophenyl-1-diazonium chloride
Chemical Formula: $C_6H_4ClN_3O_2$
Molecular Weight: 185.57

Sodium Chloride
Chemical Formula: ClNa
Molecular Weight: 58.44

Water
Chemical Formula: H_2O
Molecular Weight: 18.02

2. 1st Coupling

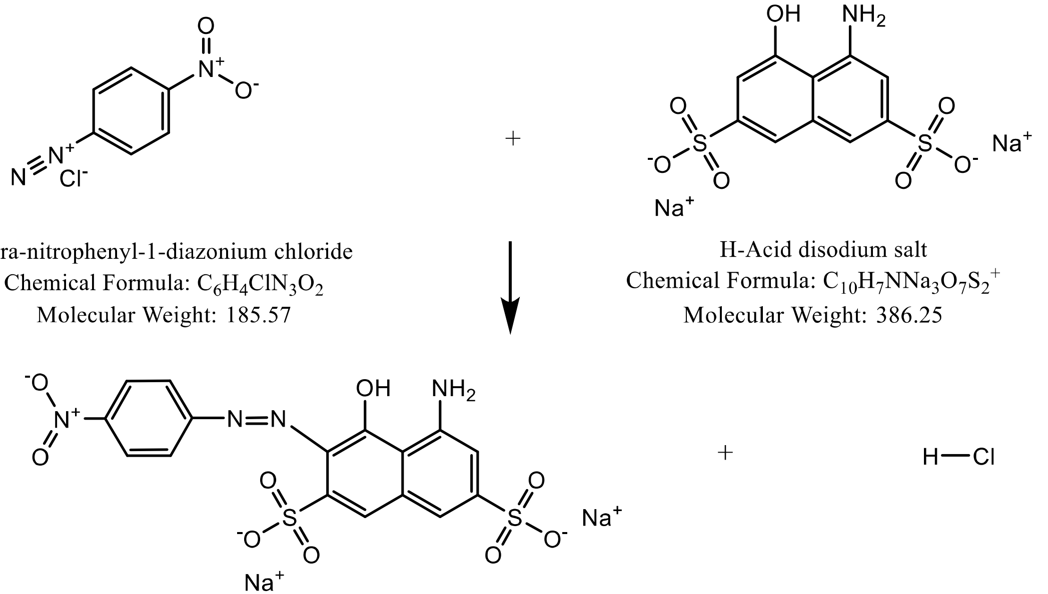


1-amino-8-naphthol-3,6-disulfonic acid (H-Acid)
Chemical Formula: $C_{10}H_9NO_7S_2$
Molecular Weight: 319.30

Sodium Hydroxide
Chemical Formula: HNaO
Molecular Weight: 40.00

H-Acid disodium salt
Chemical Formula: $C_{10}H_7NNa_3O_7S_2^+$
Molecular Weight: 386.25

Water
Chemical Formula: H_2O
Molecular Weight: 18.02



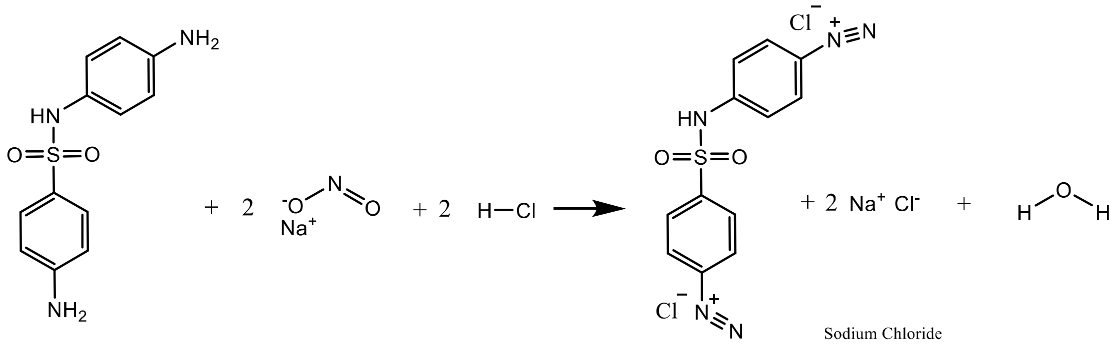
para-nitrophenyl-1-diazonium chloride
Chemical Formula: $C_6H_4ClN_3O_2$
Molecular Weight: 185.57

H-Acid disodium salt
Chemical Formula: $C_{10}H_7NNa_3O_7S_2^+$
Molecular Weight: 386.25

Mono Azo dye
(sodium 5-amino-4-hydroxy-3-((4-nitrophenyl)diazenyl)naphthalene-2,7-disulfonate)
Chemical Formula: $C_{16}H_{10}N_4Na_2O_9S_2$
Molecular Weight: 512.37

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight: 36.46

3. Diazotization of DASA



D.A.S.A.
4-Amino-N-(4-aminophenyl)benzenesulfonamide
Chemical Formula: $C_{12}H_{13}N_3O_2S$
Molecular Weight: 263.32

Sodium Nitrite
Chemical Formula: $NNaO_2$
Molecular Weight: 68.99

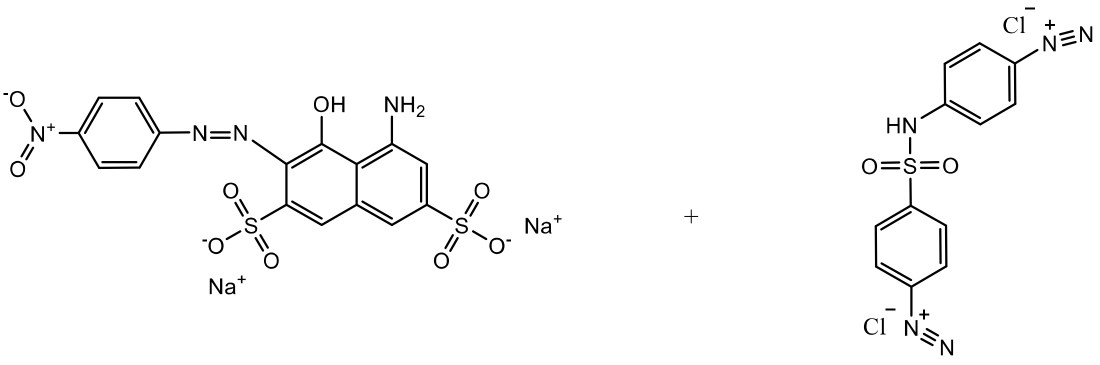
Hydrochloric acid
Chemical Formula: ClH
Molecular Weight: 36.46

Diazo salt of D.A.S.A.
Chemical Formula: $C_{12}H_9N_5O_2S^{2+}$
Molecular Weight: 358.30

Sodium Chloride
Chemical Formula: ClNa
Molecular Weight: 58.44

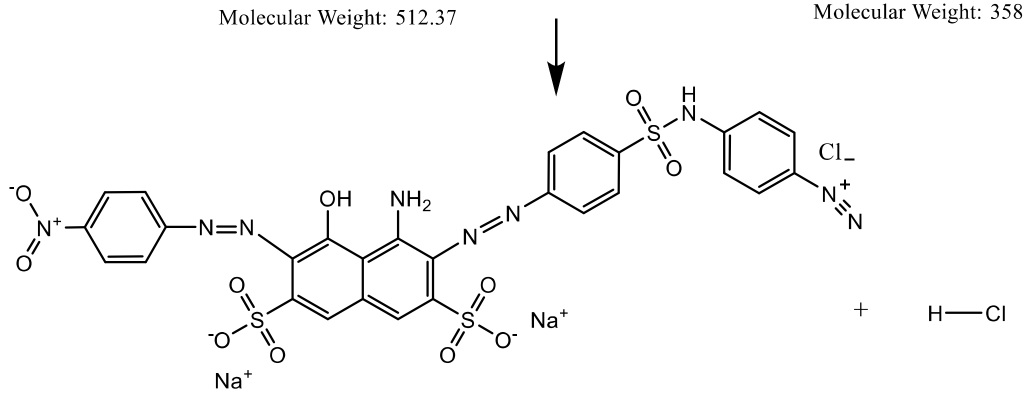
Water
Chemical Formula: H_2O
Molecular Weight: 18.02

4. 2nd Coupling



Mono Azo dye
(sodium 5-amino-4-hydroxy-3-((4-nitrophenyl)diazenyl)naphthalene-2,7-disulfonate)
Chemical Formula: $C_{16}H_{10}N_4Na_2O_9S_2$
Molecular Weight: 512.37

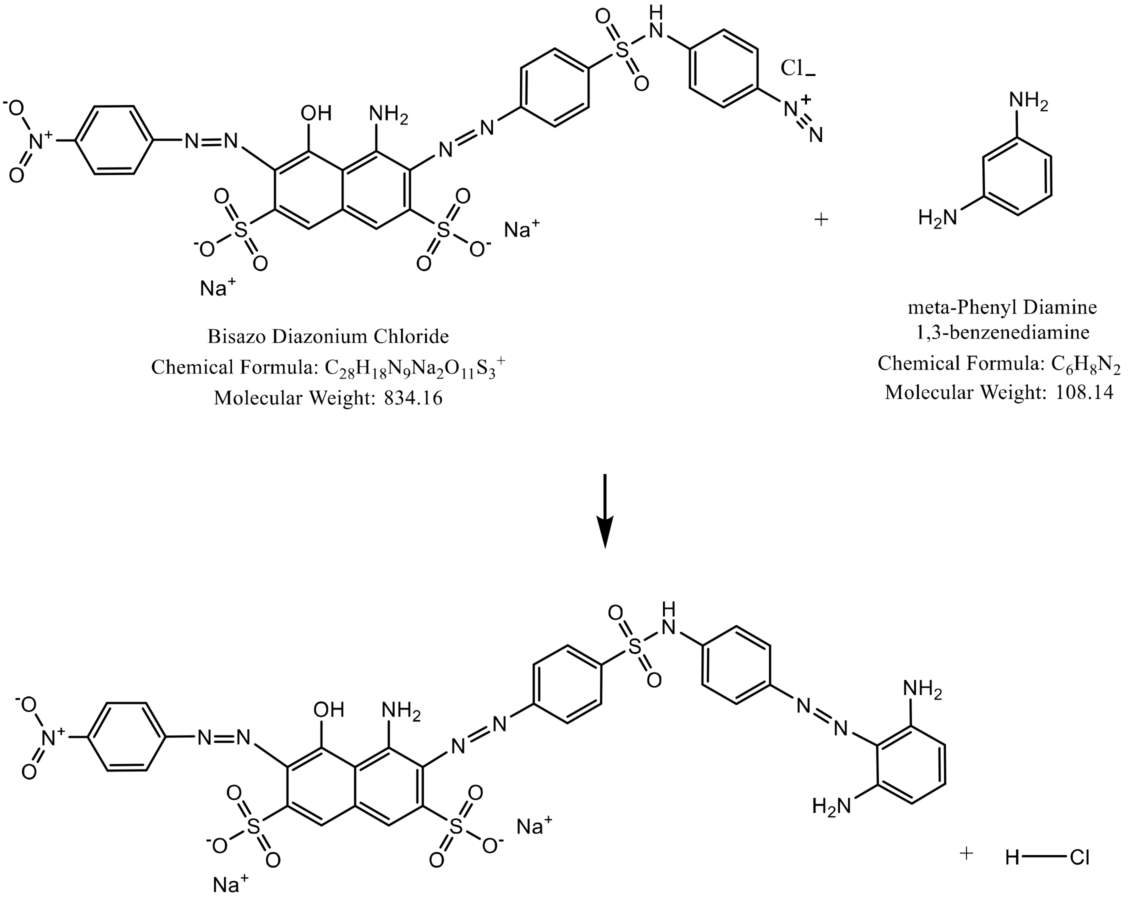
Diazo salt of D.A.S.A.
Chemical Formula: $C_{12}H_9N_5O_2S^{2+}$
Molecular Weight: 358.30



Bisazo Diazonium Chloride
Chemical Formula: $C_{28}H_{18}N_9Na_2O_{11}S_3^{+}$
Molecular Weight: 834.16

Hydrochloric acid
Chemical Formula: ClH
Molecular Weight: 36.46

5. 3rd Coupling



Bisazo Diazonium Chloride
Chemical Formula: $C_{28}H_{18}N_9Na_2O_{11}S_3^+$
Molecular Weight: 834.16

meta-Phenyl Diamine
1,3-benzenediamine
Chemical Formula: $C_6H_8N_2$
Molecular Weight: 108.14

Acid Black 210
Chemical Formula: $C_{34}H_{25}N_{11}Na_2O_{11}S_3$
Molecular Weight: 905.80

Hydrochloric Acid
Chemical Formula: ClH
Molecular Weight:
36.46

With the backdrop of the chemical equations corresponding to the reactions conducted in the production plant, the overall mass balance for the entire plant “as a production unit” is presented in **Figure 1.14**; with the basis of 1 Ton production of AB-210 at Bodal Unit VII. It is important to appreciate the significance of the systemic presentation of the production plant in the context of the stoichiometry of AB-210 synthesis. This representation is elegant on one hand and throws light on the special features associated with the inputs and outputs of the production unit on the other hand – which include the water usage as a solvent with incoming chemicals, reactant medium and cake washing, the water budget includes the amount of water consumed as a reactant as well the amount of water produced as a product of the reaction. This representation of the overall mass balance is concurrent with the mass balance-related information received from Bodal Unit VII.

It should be noted that the categorical details on the role of molecular water as a reactant as well as product in the reactions involved in synthesizing AB-210 molecule is elaborated in this analysis. **Table 1.15** depicts the detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of AB-210 at Bodal Unit VII. As presented in the Table, 1 Ton of AB-210 production also produces 241 Kg of Water (as by-product). This water, however, remains mixed with the bulk of the reacting mass in the reactor and eventually gets removed downstream through one or more unit operations.

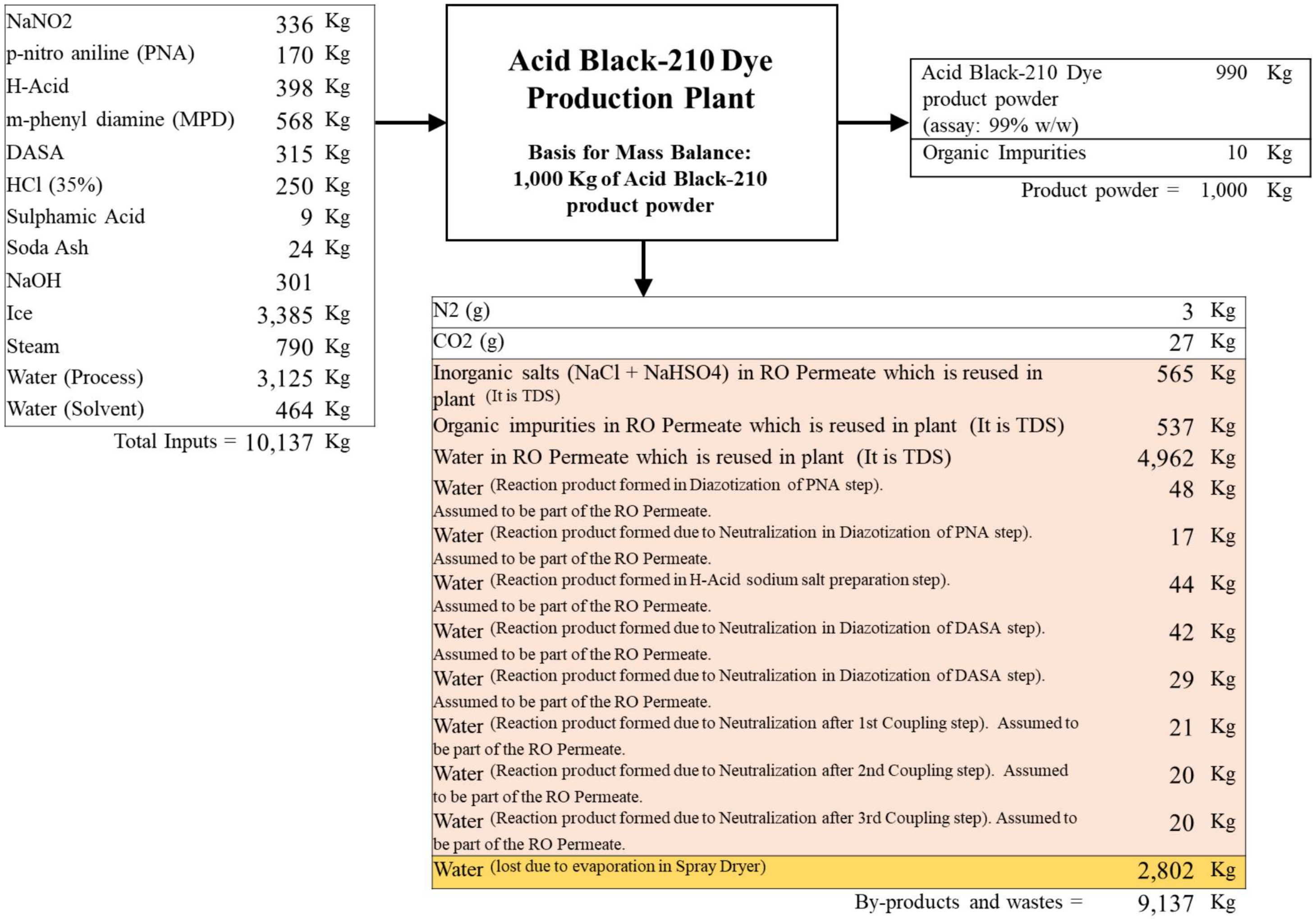
Critical Discussion on the Water Budget: Further, **Table 1.16** depicts the detailed 'Water Budget' for production of one Ton of AB-210 at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the AB-210 production plant. As presented in the Table, the overall input of water (and also the overall emission of water) is estimated to be 8.005 Ton per Ton of AB-210 production.

In summary, the net freshwater requirement works out to be 8.005 Ton of water per Ton of AB-210 production. It must be noticed that this quantity of water is essentially leaving the process plant in the form of effluent sent to ETP, moisture associated with product as well as on account of evaporation losses (see Table 1.16).

It must be noted here that, Bodal Unit VII has reported to IITB team that they reuse the permeate water from the process R.O. unit in the AB-210 production plant for reactor washing and floor flushing. The further details on the composition and concentration of this stream are provided ahead in Section 1.13 and Section 1.17. This R.O. permeate has extremely high TDS and undoubtedly will also have organic compounds and some amount of the AB-210 dye. Hence, this water will not only have a high salt content, but it will also have a dark colour – which is bound to be infeasible for recycling and even for reuse options including for floor washing and reactor flushing.

Frankly, the author of this report is critical about such "reuse actions". Even if the R.O. permeate water is used for reactor washing and floor flushing, it will eventually end up in the ETP. How the floor washing and reactor flushing undertaken with the help of the so-called R.O. permeate is achieving any cleaning? Therefore, the R.O. permeate in fact should be sent to ZLD plant and the recovered clean condensate should be used for floor washing and reactor flushing.

It is important to note here that the author of this report does not consider the claim of Bodal Unit VII regarding the reuse of the existing R.O. permeate for floor washing and reactor flushing. As a result, the mass balance of ETP, as presented in Section 1.17, presumes that the wastewater streams received at the ETP does have 99% of the mass of TDS from the dye manufacturing units (through the R.O. permeates transferred to the ETP for further treatment).



NaNO2	336	Kg
p-nitro aniline (PNA)	170	Kg
H-Acid	398	Kg
m-phenyl diamine (MPD)	568	Kg
DASA	315	Kg
HCl (35%)	250	Kg
Sulphamic Acid	9	Kg
Soda Ash	24	Kg
NaOH	301	
Ice	3,385	Kg
Steam	790	Kg
Water (Process)	3,125	Kg
Water (Solvent)	464	Kg
Total Inputs =	10,137	Kg

Acid Black-210 Dye product powder (assay: 99% w/w)	990	Kg
Organic Impurities	10	Kg
Product powder =	1,000	Kg

N2 (g)	3	Kg
CO2 (g)	27	Kg
Inorganic salts (NaCl + NaHSO4) in RO Permeate which is reused in plant (It is TDS)	565	Kg
Organic impurities in RO Permeate which is reused in plant (It is TDS)	537	Kg
Water in RO Permeate which is reused in plant (It is TDS)	4,962	Kg
Water (Reaction product formed in Diazotization of PNA step). Assumed to be part of the RO Permeate.	48	Kg
Water (Reaction product formed due to Neutralization in Diazotization of PNA step). Assumed to be part of the RO Permeate.	17	Kg
Water (Reaction product formed in H-Acid sodium salt preparation step). Assumed to be part of the RO Permeate.	44	Kg
Water (Reaction product formed due to Neutralization in Diazotization of DASA step). Assumed to be part of the RO Permeate.	42	Kg
Water (Reaction product formed due to Neutralization in Diazotization of DASA step). Assumed to be part of the RO Permeate.	29	Kg
Water (Reaction product formed due to Neutralization after 1st Coupling step). Assumed to be part of the RO Permeate.	21	Kg
Water (Reaction product formed due to Neutralization after 2nd Coupling step). Assumed to be part of the RO Permeate.	20	Kg
Water (Reaction product formed due to Neutralization after 3rd Coupling step). Assumed to be part of the RO Permeate.	20	Kg
Water (lost due to evaporation in Spray Dryer)	2,802	Kg
By-products and wastes =	9,137	Kg

Figure 1.14 Input-output analysis of Acid Black-210 dye (AB-210) at Bodal Unit VII (Basis: 1,000 Kg of AB-210 product powder)

Table 1.15 A detailed budget of the molecular water involved in the reactive steps, both, as reactant as well product of the reactions involved in the production of one Ton of Acid Black-210 at Bodal Unit VII

Role of Water in the Process Plant	**Quantity per Ton of AB-210 production (Kg)**
Water (Reaction Product) formed in Diazotization of PNA step	-48
Water (Reaction product formed due to Neutralization in Diazotization of PNA step)	-17
Water (Reaction product formed in H-Acid sodium salt preparation step)	-44
Water (Reaction product formed due to Neutralization in Diazotization of DASA step)	-42
Water (Reaction product formed due to Neutralization in Diazotization of DASA step)	-29
Water (Reaction product formed due to Neutralization after 1st Coupling step)	-21
Water (Reaction product formed due to Neutralization after 2nd Coupling step)	-20
Water (Reaction product formed due to Neutralization after 3rd Coupling step)	-20
Net Water Consumption (in reactive steps) =	**-241 ***

*241 Kg of water is generated during production of one Ton of AB-210.

Table 1.16 A detailed 'Water Budget' for production of one Ton of Acid Black-210 at Bodal Unit VII. This budget incorporates all the inputs and outputs of water with respect to the AB-210 production plant.

Role of Water in the Process Plant	**Quantity per Ton of AB-210 production (Kg)**
Input of Water (Basis: 1 Ton of AB-210)	
Water (Solvent)	464
Water (Process – used in multiple unit processes)	3,125
Water (for production of Ice)	3,385
Water (for generation of Steam)	790
Water (generated in multiple reactive steps)	241
Total input of water for one Ton of AB-210 =	**8,005**
Emission of Water (Basis: 1 Ton of AB-210)	
Water from R.O. step (reused in the process for washing)	-5,203
Water lost in Spray Drying	-2,802
Total input of water for one Ton of AB-210 =	**-8,005**
Water reused from various sources	**0**
Water leaving the system (associated with solids & evaporation loss)	**-8,005**
Net freshwater requirement (8,005 – 0 = 8,005)	**8,005**

1.13 Gap Analysis for Crude Synthetic Dyes Production

Gap refers to the space between "where we are" (the present state) and "where we want to be" (the target state). A gap analysis may also be referred to as a needs analysis, needs assessment or ***Need-Gap Analysis***.

The first step in conducting the so-called *Need-Gap Analysis* is to establish the specific target objectives by looking at the company's immediate and long term interest (mission statement, strategic goals and improvement objectives). The next step is to analyze current business processes by collecting relevant data on performance levels and how resources are presently allocated to these processes. This data can be collected from a variety of sources depending on what is being analysed. For example, by looking at documentation, conducting interviews with the experts and production managers, brainstorming and observing the production process. Lastly, after comparing the company's current state against the desirable and mandatory environmental as well as work-place safety requirements; a comprehensive plan can be developed. Such "plan" outlines the specific steps to take to fill the gap between its current and future states, and reach its target objectives.

Small and medium scale industries, in particular, can benefit from performing such *Need-Gap Analysis*. Such analysis could have the following THREE target objectives:

1. How to allocate resources?,
2. How to improve performance and profits? and
3. How to improve work-place safety and minimize environmental pollution loads?

In the following section, an effort has been made to present the improvements for short-term benefits as well as long-term benefits; based on the methodology described above.

Improvements for Short-Term Benefits

Upgradation of R.O. Units in Dyestuff Production Plant: The dyestuff manufacturing processes at Bodal Unit VII make use of R.O. systems to separate the product (dye) from the other dissolved entities and unreacted reactants. The product dyes (in the form of corresponding salts) are organic compounds typically having high molecular weight whereas the other salts have lower molecular weights. The concentrated stream from the R.O. system, thus, contains the product dye and the permeate stream contains the dissolved salts (mostly NaCl) which contribute to TDS. The permeate stream from the R.O. units is subsequently sent to the ETP for further treatment and disposal.

It is the considered opinion of the author of this report that the information reported by Bodal Unit VII on the performance of R.O. units in dyestuff production plants was either not accurate or the R.O. units provided in the production plants are not designed properly and also not operated in a scientific manner.

Neither the R.O. units can generate the so-called "permeate stream" having TDS in the neighbourhood of 20,000 mg/L (as reported by Bodal Unit VII to IITB); nor the R.O. units will produce the concentrated stream free from undesirable unreacted reactants.

Frankly, the author has not understood the operation of R.O. units (the way it was reported to IITB team). In any case, something is seriously wrong with reported performance as well as the reported composition of permeate stream.

It is evident that the R.O. systems in the production facilities for dyes will have to be upgraded to ensure that the permeate stream would not have high concentrations of dissolved salts (TDS). This can be achieved by subjecting the permeate stream to a dedicated ZLD facility in dye manufacturing plant.

This has further implications in the context of interpretation of the performance data of ETP. The first part of **Table 1.17** presents the theoretically estimated stream-wise contributions of the various sources of wastewaters received in the Equalization Tank of ETP. Also, the theoretically estimated stream-wise contributions of the wastewater streams received at the Final Tank in the ETP (before disposal) are presented in the second part of the Table. In both parts of the Table, the estimated composite concentrations are compared and contrasted with the data reported by Bodal Unit VII corresponding to the selected water quality parameter.

Table 1.17 The theoretically estimated stream-wise contributions of the various sources of wastewaters received in the Equalization Tank of ETP. Also, the theoretically estimated stream-wise contributions of the wastewater streams received at the Final Tank in the ETP (before disposal) are presented in the second part of the Table. The estimated composite concentrations are compared and contrasted with the data reported by Bodal Unit VII corresponding to the selected water quality parameter.

Sr. No.	Source of Wastewater Received in ETP Equalization Tank	Production Limit as per GPCB consent (MT/M)	Average Daily Permissible Production (TPD)	Estimated Source-wise Daily Maximum Wastewater to ETP Equalization Tank (KLD)	Estimated Source-wise TDS (mg/L)	Remarks
1	RB-5 production	1,250	41.10	35	43,100	Estimated
2	RR-195 production	500	16.44	18	62,300	Estimated
3	AB-210 production	1,250	41.10	182	119,000	Estimated
4	Boiler Blowdown	-	-	10	2,500	Estimated
5	Sewage	-	-	20	400	Estimated
	Estimated in Equalization Tank	**-**	**-**	**384**	**84,333**	**Estimated**
	Reported by Bodal Unit VII in Equalization Tank (21/10/2019)				**4,510** **This is 18 times lower than the estimated value!**	**Reported**
6	Treated stream from ETP brought to the Carbon and Sand Filter Feed Tank			384	84,333	Estimated
7	Reject stream from Boiler R.O.			60	94,600	Estimated
8	Reject stream from Sulphur Plant R.O.			0	0	Assumed
	Estimated at the outlet of the ETP	**474**		**444**	**85,719**	**Estimated**
	Reported by Bodal Unit VII at the outlet of ETP (21/10/2019)				**3,750** **This is 22 times lower than the estimated value!**	**Reported**

Significance of Temperature Control: Although the literature on the production process and efficiency improvement is limited, several Chinese patents (and a limited number of patents from other countries) are apparently available. However, owing to the issues associated with language barrier and cryptic details typically reported in patent documents, this literature did not prove to be useful in suggesting measures for improving the production processes and efficiency of Crude Synthetic Dyes production. In any case, we understand that there are several different steps, unit processes, and unit operations involved in the production of Crude Synthetic Dyes. Some of these processes need to be operated over a very slim temperature range because the raw materials and intermediates involved in the unit process are temperature sensitive.

It is well understood that the kinetics of the steps involved in Crude Synthetic Dyes production are rather complex and therefore, "manual control" of temperature proves to be inferior when compared with the so-called "automatic control". Inadequate temperature control causes the formation of unwanted isomers and side products – which eventually lead to wastage of raw materials or intermediates and, thus, lead to enhanced generation of wastewater and undesirable by-products. Needless to emphasise here that the overall yield of the desirable product, too, diminishes significantly in absence of sophisticated temperature control instrumentation – which further leads to a decrease in profits.

In view of the above kinetics-related issues, installation of the automatic temperature control instrumentation as well as sophisticated temperature measurement instrumentation are strongly recommended. Devising two separate instruments, one for automatic temperature control and one sophisticated temperature measurement is considered the best-practise for industrial chemical production. The redundancy and duplication in control and measurement instrumentation often proves to be a wise investment in the long run. Not only it improves the product yield and profits, but it also improves the process safety and decreases pollution.

Automation of Acid and / or Alkali Addition: By using a digital *p*H meter and linking it to the addition of acid / alkali in each unit process, stoichiometric addition of acid and / or alkali would be relatively easy. Thus, excessive addition of acid and / or alkali would be minimised and ultimately the quantity of salts dissolved in the reacting mass would decrease. These dissolved salts are carried forward to the treatment and finally end up in the mixed solid residue which is disposed of in CHW-TSDF. Through the closer control of *p*H in the respective reactors, especially in the Neutralization step, the generation of dissolved salts could also be minimised to a considerable extent.

The isomeric compounds and unwanted by-products are hindrances and effectively reduce the yield of Crude Synthetic Dyes production. There could be the following three reasons for the formation of unwanted isomers; while synthesizing Crude Synthetic Dyes:

a. Inherent limitations in the kinetics of various reaction stages which ultimately lead to the formation of isomers,

b. Improper control of reaction parameters like temperature, pressure, *etc.*, and

c. Excessive usage of acids and alkalis starting from sulphonation to final Neutralization step. Due to this, sodium salts (typically NaCl) get accumulated in the crude Crude Synthetic Dyes slurry, further inhibiting the separation rate of Crude Synthetic Dyes.

In view of the above thermodynamic and kinetics-related issues, installation of the sophisticated digital *p*H control instrumentation as well as automated systems for acid / alkali addition are strongly recommended. Devising two separate systems, one for sophisticated *p*H control and one for automated addition is considered the best-practise for industrial chemical production. The redundancy and duplication in these systems often proves to be a wise investment in the long run. Not only it improves the product yield and profits, but it also improves the process safety and decreases pollution.

Significance of Digital Flowmeters to Track Water Usage: As seen in the water budget, production of Crude Synthetic Dyes is highly water-intensive. Keeping a track of water at every input and the output is essential from the point of view of having an accurate water balance and water budget. Currently, since there is no flow meter to keep track of the water usage, the values of the water usage are rough estimates. This is unacceptable. In order to have a perfect mass balance and water balance, every part of the water used in the plant needs to be tracked.

Therefore, the use of digital flowmeters at all the places in the plant where water is used is recommended. The planning and implementation of this recommendation should be expedited and taken up as the first priority.

Housekeeping and Maintenance: The investigation team from IIT Bombay visited this plant several times and discussed with persons from Production and Environment Protection teams. There was a great cooperation from these persons and the information was furnished efficiently through emails, completing the requested tabulated information, cooperating with the personnel from Vadodara Enviro Channel Limited (VECL) while collecting samples and obtaining data as well as through face-to-face interactions during the site visits. The IIT Bombay team is grateful to the company for the help and facilitation.

Frankly, whenever IIT Bombay team visited the production facility as well as ETP and STP, *prima facie* it appeared as though the overall upkeep and housekeeping was visibly poor. Most of the floors and surfaces inside the roof and columns of the shed were unclean, rusted and it was clear that the housekeeping related functions were generally given a low priority.

It is generally understood that the functions related to routine maintenance of equipment, reactors, piping, loading-unloading platforms, and staircases (ladders) become difficult and the overall surroundings have poor housekeeping. It is also understood that the frequency of maintenance, too, increases in the midst of unclean surroundings (more corrosion, frequent breakdown, difficulty in repairs and maintenance).

More importantly, the propensity for accidents, fire, explosion, injury at the workplace are generally found to enhance in the situations where overall maintenance and housekeeping is poor. The modern safety science, in fact, has been lately recommending for superlative interventions related to cleanliness, daily upkeep, and above all, the "preventive maintenance".

Maintenance and calibration of all instrumentation and control hardware is of utmost importance, not only from the point of view of the production process and product purity but also from the point of view of minimization of pollution and enhancement of health and safety of the workers. Poorly or rarely calibrated instrumentation and control hardware will often lead to addition of an incorrect amount of inputs to the reactor or give a false picture of the conditions in the reactor. This might, in turn, impact the indoor air quality, safety of the workers, and generation of pollution from the production plant. If the production plant is not properly maintained, the probability of malfunctioning of the instrumentation and process control devices would increase. Also, the functioning of ETP and STP will get affected beyond the certain extent of negligence in the production plant.