



## HAZARD IDENTIFICATION AND CONTROL IN PESTICIDES INDUSTRY

Karthikeyan V<sup>[1]</sup> Sivaguru S<sup>[2]</sup>

<sup>[1]</sup> ASSISTANT professor, Department of mechanical Engineering, Knowledge institute of Technology

Kakapalayam, Salem-637504, Tamilnadu

<sup>[2]</sup> Student, Department of Industrial Safety Engineering, Knowledge institute of Technology

Kakapalayam, Salem-637504, Tamilnadu

**1. Abstract—** Safety plays an important role in human beings' life. Occupational health and safety become a vital part in every Industry. The background of this project is to condense the cause and effects in health and safety & environment. The main objective of this paper is to identify the hazards in pesticide manufacturing industry which may affect the employer and the environment. To assess the safety means, it needs to reduce the risk everywhere, so that Hazard Identification and Risk Assessment (HIRA) can be done for working in a Effluent treatment plant in pesticides industry. To find the hazards means, then risk can be accessed from the hazards and then to analyse the severity rating for the hazards. Calculating the severity and probability of occurrence and suggesting the hazards are acceptable or not acceptable. By using the Chemical exposure level meter or quality analyse the organic and inorganic content present in all effluent stream from plant. We can evaluate the Hazard exposure limit while working Effluent treatment plant. These Chemical are hazardous to human health. So, we have to reduce and control the hazards by using Risk assessment. The project work focuses on using the HIRA technique on improvement of health and safety while working in Pesticide manufacturing industry.

**Keywords—**Effluent treatment plant, Pesticides manufacturing process, Minimum explosion concentration, Hazard identification and risk assessment.

### 2. INTRODUCTION

Safety plays an important role in human beings' life. Occupational health and safety become a vital part in every Industry. The background of this project is to condense the cause and effects in health and safety environment. The main objective of this paper is to identify the hazards in pesticide manufacturing industry aqueous treatment in Effluent treatment plant which may affect the employer and the environment. To assess the safety means, it needs to reduce the risk everywhere, so that Hazard Identification and Risk Assessment (HIRA) can be done for working in a Effluent treatment plant in Pesticide manufacturing industry. To find the hazards means, then risk can be accessed from the hazards and then to analyse the severity rating for the hazards. Calculating the severity and probability of occurrence and suggesting the hazards are acceptable or not acceptable. By using the Volatile organic content meter or quality analysis report for individual aqueous receiving from plant. Chemical exposure limit while working

Effluent treatment plant These Chemical are hazardous to human health. So, we have to reduce and control the hazards by using Risk assessment. The project work focuses on using the HIRA technique on improvement of health and safety while working Effluent treatment plant e.

### PROCESS

**THE Bromination of RRCMA Reaction conditions / Operation details:** Aluminium chloride catalyst is taken in solvent EDC and stirred for 30 minutes. The mass is cooled to 5.0°C. RR CMA is dissolved in EDC and this solution mixed with the above in 1-hour period keeping the temperature between 5.0 - 7.5°C. Dry HBr is passed over 6 - 8 hours into the above reaction mixture maintaining the temperature again at 5.0 - 7.5°C. the reaction mass is stirred for 30 minutes after HBr addition and nitrogen is passed through the reaction for 30 minutes to drive off unreacted HBr. Unreacted HBr coming out during the reaction and purging is absorbed in water and can be sold.

The reaction mass is drowned into ice and dilute hydrochloric acid mixture Slowly keeping the temperature between 0.0 to 5.0°C the mass is then stirred, temperature raised to 25.0°C, settled and the layers separated. The aqueous layer containing 30% Aluminium chloride can be sold to zeolite and alum manufactures and hydrochloric acid is washed with mild hydrochloric acid to remove traces of Aluminium chloride. The organic layer is then treated with dilute caustic lye solution and water to convert the bromo acids into sodium salt of bromo acids and tri bromo acid to desired di bromo acids into sodium salt of bromo acids and tri bromo acid to desired di bromo acids by dehydrohalogenation. The mass is settled and layers are separated. The mass is then cooled to 30.0°C and filtered to obtain crude be thermic acid. The purity of CMA used is above 99.00% and that of key raw materials like Aluminium chloride, HBr and EDC are above 98.00%. The purity of becisthemic acid obtained will be between 88.9°C and the associated impurities are choro bromo acid and unreacted CMA. During this process Sodium bromide and hydrogen bromide aqueous generated. In this Aqueous create the health and safety environmental incident in pesticide manufacturing industry.

### 3...Problem identification

. Employees in the pesticide manufacturing sector neutralizing the wastewater during treatment. While dealing with the potential risks and the strong fumes produced, neutralizing the aqueous is also highly challenging. It has multiple effects on risky acts and conditions that affect humans. Ejector spares are also damaged as a result of severe corrosion and erosion in stainless steel evaporators. The product has performed a risk analysis for hazardous identification. Study by Hazop is also accessible.

1. When managing untreated Bromination aqueous in effluent treatment plants, HIRA studies are used to document and monitor environmental incidents as well as unsafe acts, unsafe conditions, close calls, risk-related activities, and investigation processes.
2. Aqueous is naturally very acidic when not handled. Because there is insufficient mole bromine to complete the reaction, free bromine is present in the aqueous.
3. Additionally challenging and producing heavy fumes when neutralizing the aqueous. Hazardous environmental conditions, risky behavior, etc.
4. Due to severe corrosion and erosion, the Multiple Effect Evaporator composed of stainless steel would corrode and the spare ejectors will be damaged.
5. The product has performed a risk analysis for hazardous identification.
6. For recording and monitoring the Environmental incident and unsafe acts, unsafe conditions, near miss and risk related activities and investigation process while handling of untreated Bromination aqueous in Effluent treatment plants.
7. Untreated Aqueous is highly acidic nature.
8. Free Bromine Present in the Aqueous because Excess Mole Bromine Required for Reaction Completion.
9. While neutralizing the aqueous also very difficult and heavy fumes generated during neutralization.
10. Environmental Hazardous and unsafe condition and unsafe act.
11. Multiple Effect Evaporator made for Stainless steel it will be Corroded and Ejectors spares also damage due to highly corrosion and Erosion.
12. Hazardous identification risk analysis done by the product.
13. Hazop study document also available.

### 4. OBJECTIVE

#### Objective of the Project

The handling of bromination stage aqueous at the effluent treatment plant in order to reduce safety and environmental incidents in the pesticide production business. Keeping track of all reports, recording harmful acts, unsafe circumstances, near-misses, risk-related activities, and investigation processes.

To perform the appropriate control measures while handling the recovery system and measure input Quality and Quantity parameter and Output Quality and Quantity parameter. To identify the potential risks in the aqueous generated by the pesticide industry.

. 1. To minimize the Safety and Environmental incident in pesticides industry in Effluent treatment plant while handling of Bromination stage aqueous. Everyday Safety team Recording and monitoring the unsafe acts, unsafe conditions, near miss and risk related activities and investigation process and to maintain all reports.

2. To Recover the Bromine from this aqueous before sending the Effluent treatment plant.

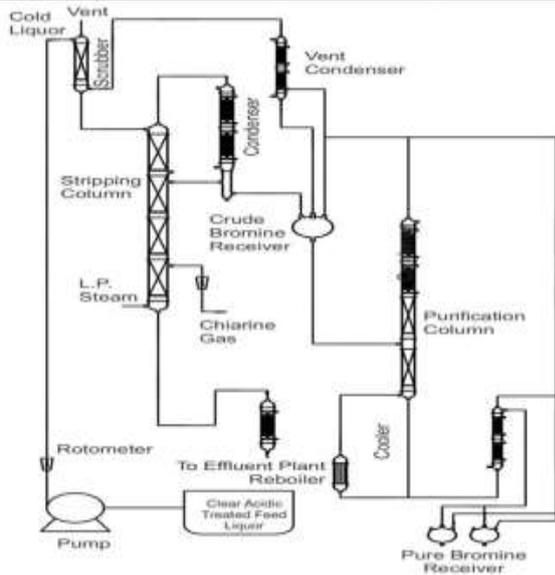
3. To take necessary control measures handling Recovery system and measure input Quality and Quantity parameter and Output Quality and Quantity parameters.

4. To make Standard operating procedure and Batch Manufacturing Record for Bromine Recovery system with approval of Quality Assurance and Quality control department.

### 5. Methodology

1) Hazard identification, risk assessment and control are an on-going process. Therefore, regularly review the effectiveness of your hazard assessment and control measures. Make sure that you undertake a hazard and risk assessment when there is change to the workplace including when work systems, tools, machinery or equipment changes. Provide additional supervision when the new employees with reduced skill levels or knowledge are introduced to the workplace. The phase of risk identification is essential, because it establishes the bases of the risk analysis. Indeed, the data of risk identification will be the input of the evaluation phases. Therefore, it is necessary to make an identification phase in an exhaustive way to get the best results.

2) HIRA is highly dependent on the availability and accuracy of the input data, when provided with complete Input data, a higher confidence on the validity and robustness of the results are obtained. The example of data collection will be specific to operations, building design, personnel / population occupancy levels. HIRA Risk Assessment is employed for risk management and safety improvement in several industries. It provides a quantitative assessment of potential risks known and provides a basis for evaluating process safety with reference to a planned risk acceptance criterion.



Process flow chart for Bromine recovery system.

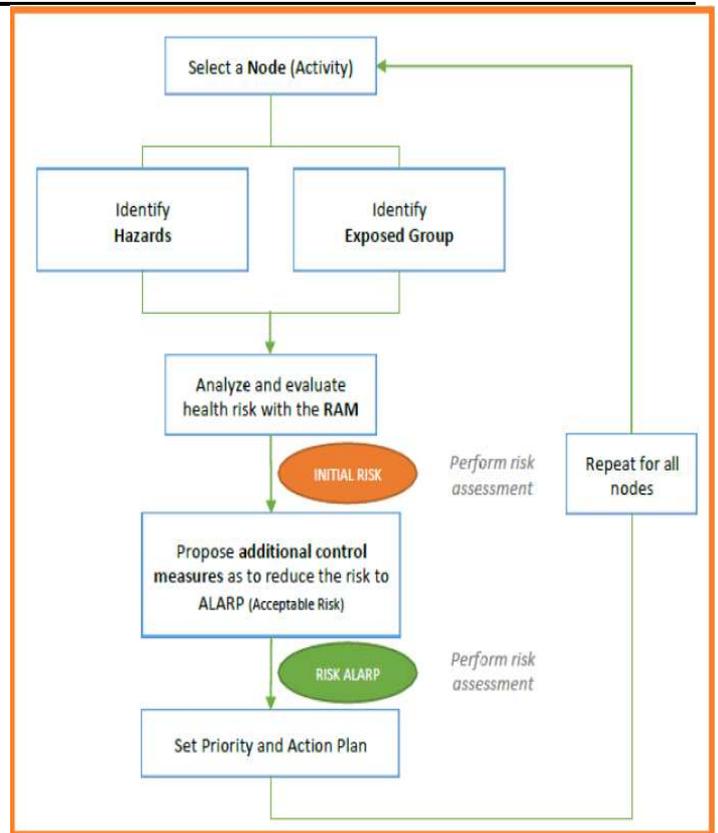
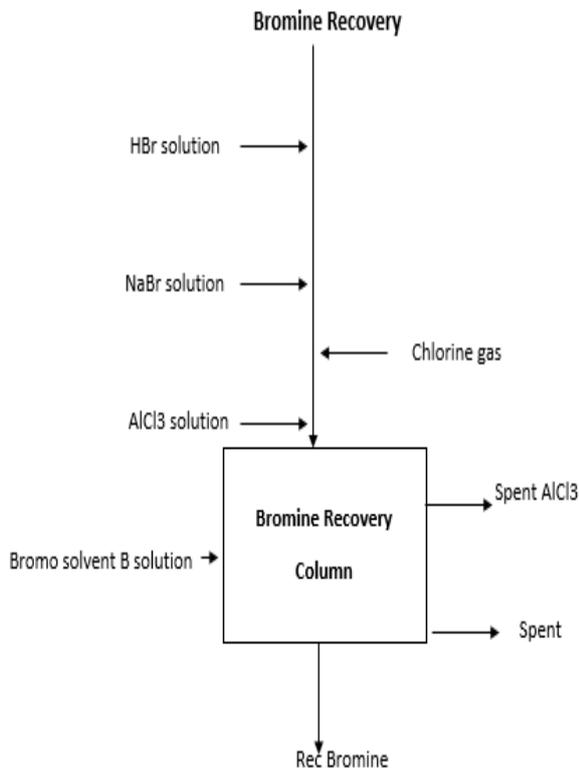


Fig. 1 HIRA Flow Chart



A. HIRA Flow Chart

*E. Risk Matrix*

For each of the identified hazard, the level of risk is assessed based with Risk Assessment Matrix during HIRA review. Risk ranking is firstly performed based on the unmitigated risk for each hazard, and then the level of risk is re- evaluated after taking into consideration of the existing prevention/mitigation measures and controls

PROBABILITY	Incident severity				
	1 Very low	2 Low	3 Medium	4 High	5 Very high
5 Permanently to happen	Medium	Medium	High	High	High
4 Very probably to happen	Medium	Medium	Medium	High	High
3 Probably to happen	Low	Medium	Medium	Medium	High
2 Unlikely to happen	Low	Low	Medium	Medium	High
1 Randomly to happen	Low	Low	Low	Medium	Medium

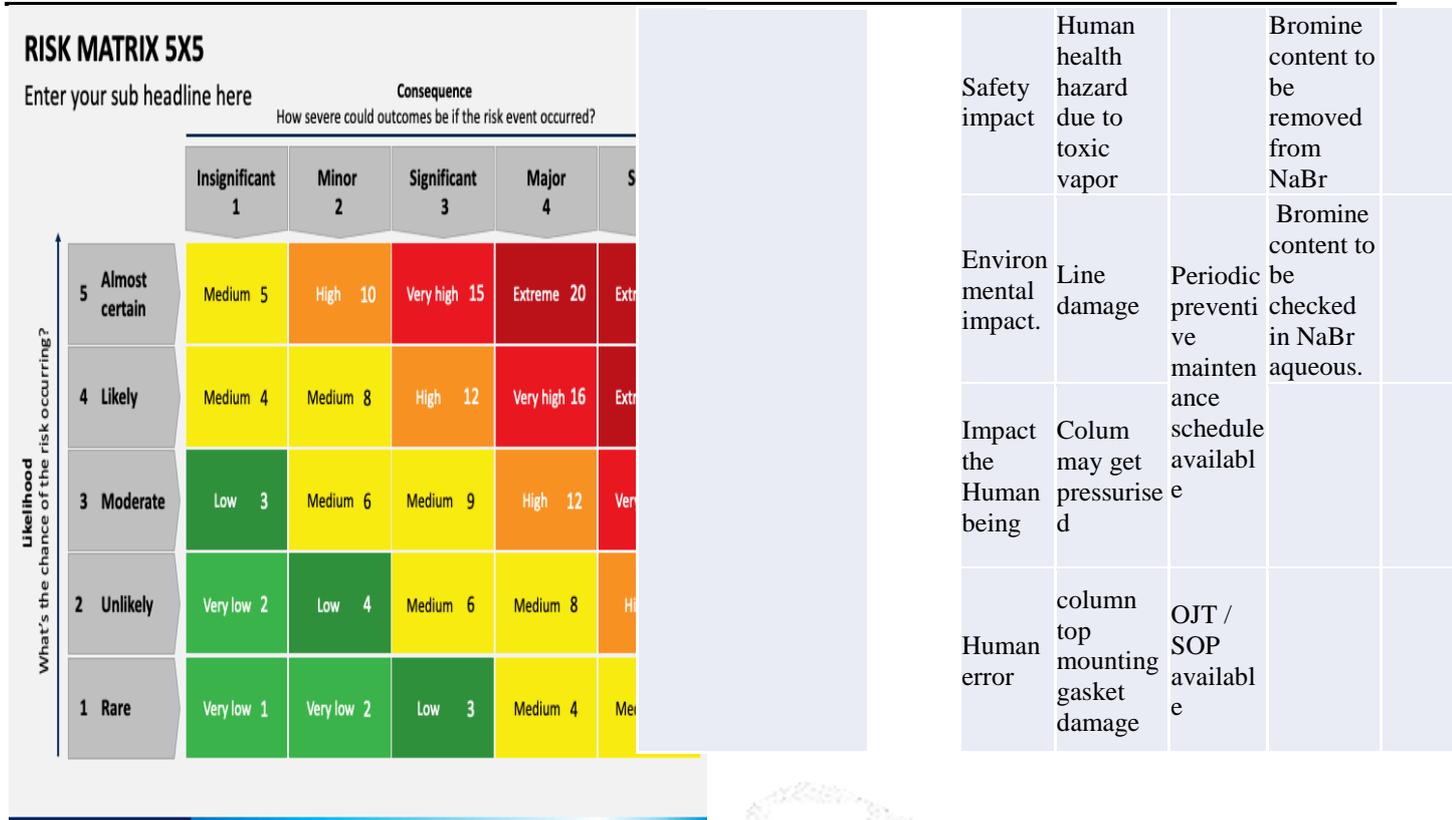


Fig. 2 Risk Matrix

If the risk is in the Green region, the risk is acceptable and no further action is required. If the risk is in the Yellow region, risk is in tolerable regions and needs to be demonstrated to be as Low as Reasonably Achievable by recommending further action. If the Risk is still in the Red region, this is not acceptable and action definitely needs to be taken. HIRA Review team shall discuss the proposed actions, where applicable, to address the hazard that is ascribed with a medium to high-risk rating.

**RISK ASSESSMENT IN AQUEOUS HANDLING IN MULTIPLE EFFECT EVAPORATOR**

**BROMINE RECOVERY SYSTEM**

- First open the feed valve and start feed at the flow rate of 400-500kg/hr. into the column.
- Then open the steam valve slowly and raise column bottom temperature to NMT-85.0°C and top temperature to NMT-90.0°C.
- Once the column top temperature reaches NLT-65.0°C, increase the feed flow rate to 1000±500 Lit/hr.
- Open chlorine tonner valve and feed valve and start feeding chlorine gas into the column. Flow rate of chlorine gas should be 50±20 kg/Hr.

- After starting chlorine gas addition, bromine gas starts to the primary condenser where it will be condensing with the help of cooling water and uncondensed bromine will go to the secondary condenser with chilling water.
- Condensed bromine + water will enter to the phase separator. Initially, the side overflow line of bromine from the bottom to be kept closed to build up the bromine level and to make the bromine seal.
- The top layer of bromine water will go back to the column. Once the bromine seal will be made, then open the side overflow valve and bromine will continuously overflow to the top of purification column.
- Once the level of bromine fills in up to top of reboiler, close reboiler bottom to collection flask valve.
- Start heating the bromine into purification column and achieve the 40°C temperature by adjusting the steam. Once temperature achieved open the reboiler top to collection flask valve. Maintain the temperature of reboiler at 40.0°C-50.0°C.
- The pure bromine is continuously collected in 20 liter bromine collection flask. During Reaction time temperature

**HAZOP WORKSHEET**

Node NO.:	MEE System	P&ID NO.:	TAG/CUD/DMT/04
Node Description:	Halex Reaction	Design Intention :	Stainless steel, DP- 1.0 kg/cm2, DT-80 to 100°C flow 15 kg/cm2
GUIDE WORD	DEVIATION	CAUSES	CONSEQUENCES
BROMINE CONTENT HIGHER IN NaBr and HBR	Temperature	Fast Heating	MEE column get damage PG, TI available in jacket header
			Material bromine vapour Evolved emission

should be maintained bottom temperature at 95.0°C-105.0°C and column top temperature at 80.0°C-90.0°C.



Fig.1 Bromine Recovery process flow chart.



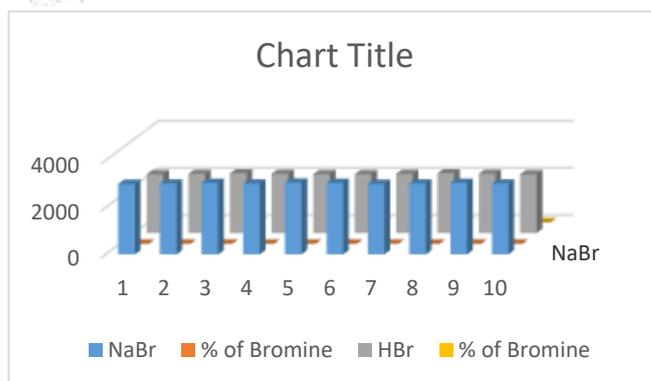
6	Composition	Water - 90.0%, Inorganic impurities like NaCl, NaNO <sub>3</sub> , CaCl <sub>2</sub> & Organic impurities — 2%	Water - 85.0%, Inorganic impurities like NaCl, NaNO <sub>3</sub> , CaCl <sub>2</sub> & Organic impurities — 2%	Water - 78%, Inorganic impurities like NaCl, NaNO <sub>3</sub> , CaCl <sub>2</sub> & Organic	Water - 88.0%, Inorganic impurities like NaCl, NaNO <sub>3</sub> , CaCl <sub>2</sub> & Organic impurities — 2%
---	-------------	--	--	--	--

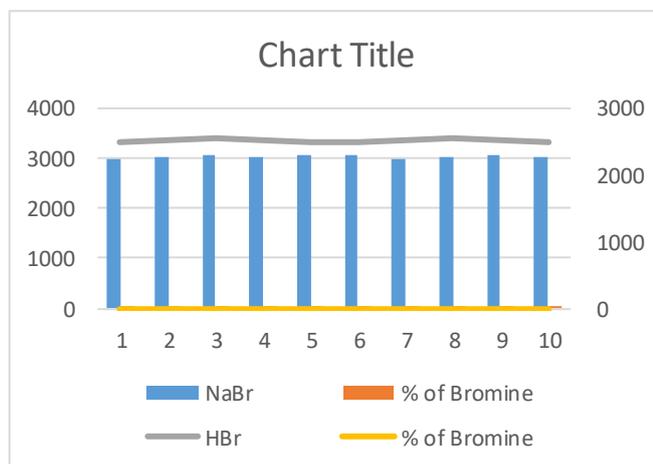
**RESULT AND DISCUSSION**

Aqueous generation Quantity & Quality details(Before Recovery)				
S.no	NaBr	% of Bromine	HBr	% of Bromine
1	3000	17.0%	2500	15.0%
2	3020	15.0%	2520	15.2%
3	3050	16.0%	2540	15.5%
4	3020	15.5%	2520	15.5%
5	3060	16.5%	2500	15.3%
6	3050	17.0%	2500	15.0%
7	3000	15.0%	2520	15.0%
8	3020	16.0%	2540	15.2%
9	3050	15.5%	2520	15.5%
10	3020	16.5%	2500	15.5%

**6.DATA COLLECTION**

S. No	Characteristics	NaBr	AlCl <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	HBr
1	Physical State	Liquid	Liquid	Liquid	Gas
2	Colour	Colourless	Colourless	Colourless	Colourless
3	PH	6.5-8.5	1.5-2.5	1.5-2.5	1.5-2.5
4	Odour	Odourless	Odourless	Pungent	Odourless
5	Chemical	NaBr-10.0%	AlCl <sub>3</sub> -12.0%	NH <sub>4</sub> Br-20.0%	HBr-12.0%





The bromine content percentage was lowered from 15% to 2% based on bromine recovery data from aqueous before and after treatment in a glass recovery column. As a result, the risks and dangers associated with pesticide manufacturing are reduced.

## 8. CONCLUSIONS

Chemical companies face difficulties controlling the effluent from these sites since process plants discharge organic and inorganic substances into the water. We have highlighted the risks, such as potential human injury, that must be addressed by engineering control since the hazards produced during heating and neutralisation in aqueous wastewater treatment plants affect both humans and the environment. Use the bromine recovery procedure and refer to the journals. The Tabular column above provides an example of how to reduce hazards both before and after treatment. These study papers have led us to conclude that HIRA recommendations should be the basis for the administration of the bromine recovery system.

## 9. SCOPE OF THE FUTURE WORK

The following hazards are in different workplaces at different sites while carrying different activities such as manual handling, Raw material Charging and transferring and during reaction and Reactor maintenance, work at height, welding work, electrical maintenance, mechanical maintenance, boiler maintenance, chemical handling, weather conditions, etc.,

While carry out a works, we have to eliminate the hazards, for that we have to take a correct control measures for concern activities. The few control measures are mentioned below.

- 1) Standard operating procedure.
- 2) Batch Manufacturing Record.
- 3) Administration control and Engineering Control
- 4) Work Permit.
- 5) Ensure cleanliness of work area
- 6) Ensure water / Grease or any contamination of floor area is clear.

## Aqueous generation Quantity & Quality details(After Recovery)

S.no	NaBr	% of Bromine	HBr	% of Bromine
1	3000	3.0%	2500	1.6%
2	3020	1.5%	2520	3.0%
3	3050	1.6%	2540	1.5%
4	3020	2.5%	2520	1.6%
5	3060	1.6%	2500	2.5%
6	3050	3.0%	2500	1.6%
7	3000	1.5%	2520	3.0%
8	3020	1.6%	2540	1.5%
9	3050	2.5%	2520	1.6%
10	3020	1.6%	2500	2.5%

- 7) Two-man operation required.
- 8) Ladders / Steps / Scaffolding are registered and compliant
- 9) Ensure isolation of area for operations.
- 10) Ensure use of Mechanical Assistance.
- 11) Ensure Equipment is registered and Compliant.
- 12) Ensure MSDS is available, and controls are there.
- 13) Ensure PPE is suitable and sufficient to hazards identified when PPE used as a control measure.
- 14) Ensure electrical isolations have been made
- 15) Ensure guards on moving machinery are in place
- 16) Ensure portable tools are in good condition and compliant
- 17) Ensure adequate training is provided

## 10. REFERENCE

1. Arsenyeva O., Tovazhnyansky L. L., Kapustenko P., Khavin G., 2011, Optimal design of plate-and-frame heat exchangers for efficient heat recovery in process industries, Energy, 36, 4588-4598.
2. Boldyryev S., Varbanov P. S., Nemet A., Kapustenko P., Klemeš J. J., 2013, Targeting Minimum Heat Transfer Area for Heat Recovery on Total Sites. Chemical Engineering Transaction, 35, 79-84.

3. Boldryev S., Varbanov P. S., Nemet A., Klemeš J. J., Kapustenko P., 2013, Capital Cost Assessment for Total Site Power Cogeneration. *Computer Aided Chemical Engineering*, 32, 361-366.
4. Davenport, R.E. 2003. Bromine: CEH product review. In *Chemical Economics Handbook*. Menlo Park, CA, USA: SRI Consulting.
5. Harben, P. 2003. Bromine. *Mining Engineering* 55(6):18–20.
6. Klemeš J., Friedler F., Bulatov I., Varbanov, P. 2010, Sustainability in the process industry – Integration and optimization. New York: McGraw-Hill., USA, 362 p.
7. Klemeš J., Dhole V.R., Raissi K., Perry S.J., Puigjaner L., 1997, Targeting and Design Methodology for Reduction of Fuel, Power and CO<sub>2</sub> on Total Sites, *Applied Thermal Engineering*, 17, (8-10), 993–1003.
8. Ober J. A., 2013, U.S. Geological Survey, Mineral Commodity Summaries.
9. Smith R., 2005, Chemical process design and integration, Chichester, UK: Wiley.
10. Tovazhnyansky L., Kapustenko P, Ulyev L., Boldryev S., 2011, Heat Integration Improvement for Benzene Hydrocarbons Extraction from Coke-Oven Gas. *Chemical Engineering Transaction*, 25, 153-158.
11. Tovazhnyansky L., Kapustenko P, Ulyev L., Boldryev S., 2009, Synthesis of energy saving integrated flowsheet for sodium hypophosphite production. *Chemical Engineering Transactions*, 18, p. 93-98.
12. D Koh, T-C Aw (2003) Surveillance In Occupational Health. *Occup Environ Med* 2003; 60:705–710.
13. N.S. Arunraj, J. Maiti (2007) Risk-based maintenance—Techniques and applications. *Journal of Hazardous Materials* 142 (2007) 653–661.
14. Małgorzata Pe cillo (2016) The resilience engineering concept in enterprises with and without occupational safety and health management systems. *Safety Science* 82 (2016) 190–198.
15. Gabriele Baldissone, Lorenzo Comberti, Serena Bosca, Salvina Murè (2018) The analysis and management of unsafe acts and unsafe conditions. Data collection and analysis. *Safety Science*,
16. Michael O’Toole (2002) The relationship between employees’ perceptions of safety and organizational culture. *Journal of Safety Research* 33 (2002) 231–243.
17. Weast, Robert (1984). CRC, Handbook of Chemistry and Physics. Boca Raton, Florida: Chemical Rubber Company Publishing.pp. E110. ISBN 0-8493-0464-4.
18. Kondev, F. G.; Wang, M.; Huang, W. J.; Naimi, S.; Audi, G. (2021). "The NUBASE2020 evaluation of nuclear properties" (PDF). *Chinese Physics C*. 45 (3): 030001. doi:10.1088/1674-1137/abddae.
19. Ballard, Antoine (1826). "Memoir on a peculiar Substance contained in Sea Water". *Annals of Philosophy*. 28: 381–387 and 411–426. Archived from the original on 17 July 2021. Retrieved 5 June 2020.
20. Landolt, Hans Heinrich (1890). "Nekrolog: Carl Löwig". *Berichte der deutschen chemischen Gesellschaft*. 23 (3): 905–909. doi:10.1002/cber.18900230395. Archived from the original on 9 February 2022. Retrieved 24 February 2022.
21. Barger, M. Susan; White, William Blaine (2000). "Technological Practice of Daguerreotypy". *The Daguerreotype: Nineteenth-century Technology and Modern Science*. JHU Press. pp. 31–35. ISBN 978-0-8018-6458-2.
22. "Bromine 207888". Sigma-Aldrich. 17 October 2019. Archived from the original on 25 July 2021. Retrieved 21 December 2021
23. Samuel Hopkins Adams (1905). The Great American fraud. Press of the American Medical Association. Retrieved 25 June 2011
24. Samuel Hopkins Adams (1905). The Great American fraud. Press of the American Medical Association. Retrieved 25 June 2011