Process Characterization:
Materials Accounting

What's Involved?

STEP 1: Process mapping
- identify processes
- define WHERE inputs enter
- define WHERE outputs leave
- chemical pathway analysis

QUALITATIVE

STEP 2: Production Unit Info
- identify PURPOSE OF TOXIC
- identify PRODUCT
- identify PRODUCTION UNIT
- identify UNIT OF PRODUCT

STEP 3: Materials accounting
- define HOW inputs are used
- define HOW outputs leave
- define prices/volumes
- identify losses

QUANTITATIVE

Process Characterization

For each toxic chemical used, identify and characterize:

- **Purpose**
- **Total amounts and amounts per unit of product**
- **Byproduct fate:** amounts released on-site, treated on-site and off-site, recycled on-site and off-site, and disposed of on-site and off-site
- **Emissions to each media:** amounts released on-site, disposed on-site, transferred off-site, and treated, recycled and disposed of off-site to air, surface water, ground water, and land
- **Cost of toxics** (qualitative or quantitative)
  - **Quantitative** if technically feasible options identified
  - **Qualitative** if no technically feasible options identified

Byproducts Represent Inefficiency

- Piped to onsite air, water, or waste treatment systems
- Collected as hazardous or solid waste
- Emitted directly to the air
- Recovered and re-introduced into the production unit
- Sold, traded, or entered into commerce

Emissions

Emissions: Byproducts that are released to the environment OR are transferred to an onsite or offsite management facility

Emissions = Total byproduct – quantity of byproduct destroyed in onsite treatment

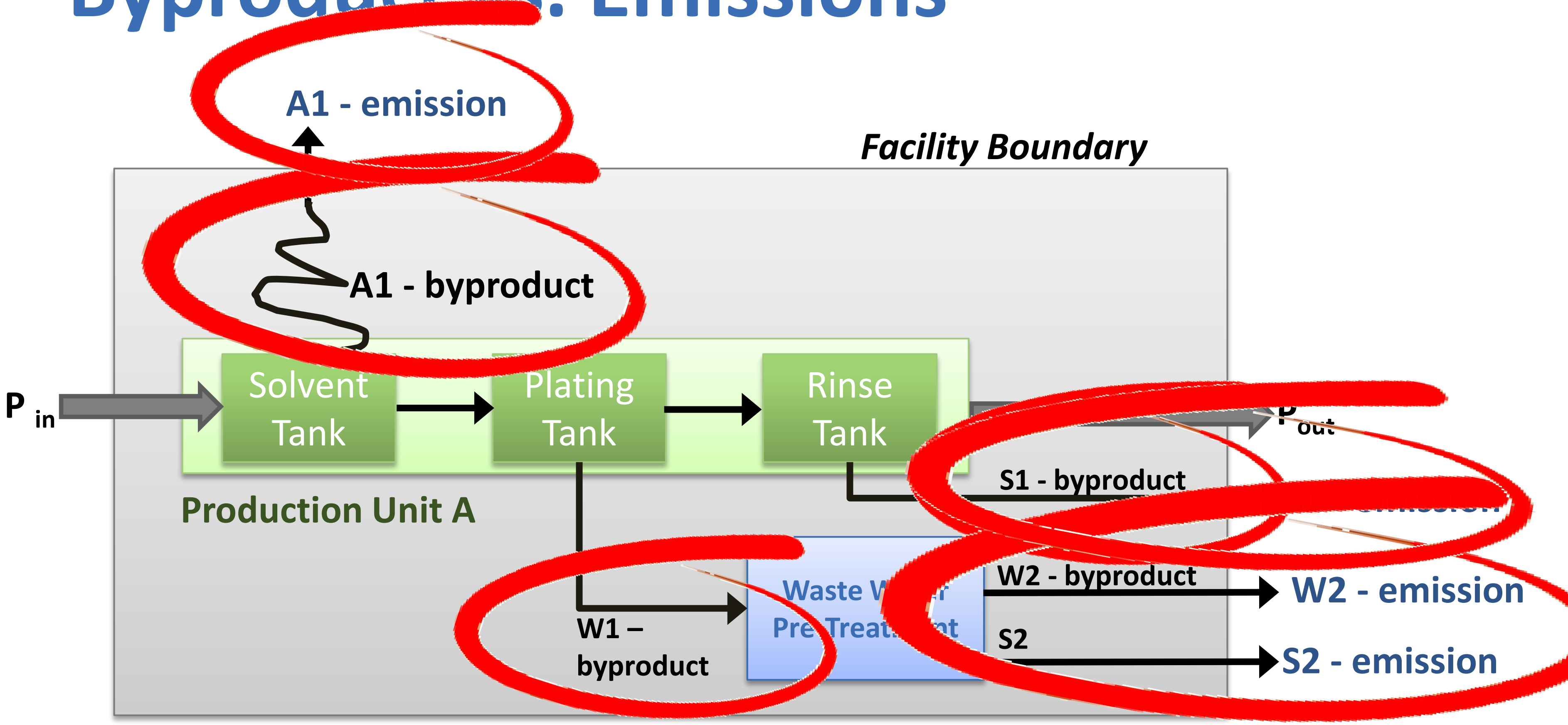
Outputs to onsite treatment or recycling = Byproduct

Outputs to the environment from onsite treatment or recycling = Emission

Emissions include:

- Air (Point and Fugitive)
- Waste Water (to POTW, surface water, ground water, etc.)
- Surface water, ground water (storm drains)
- Hazardous and Solid Wastes sent to Waste Management Facilities
- Off-Site Recycling

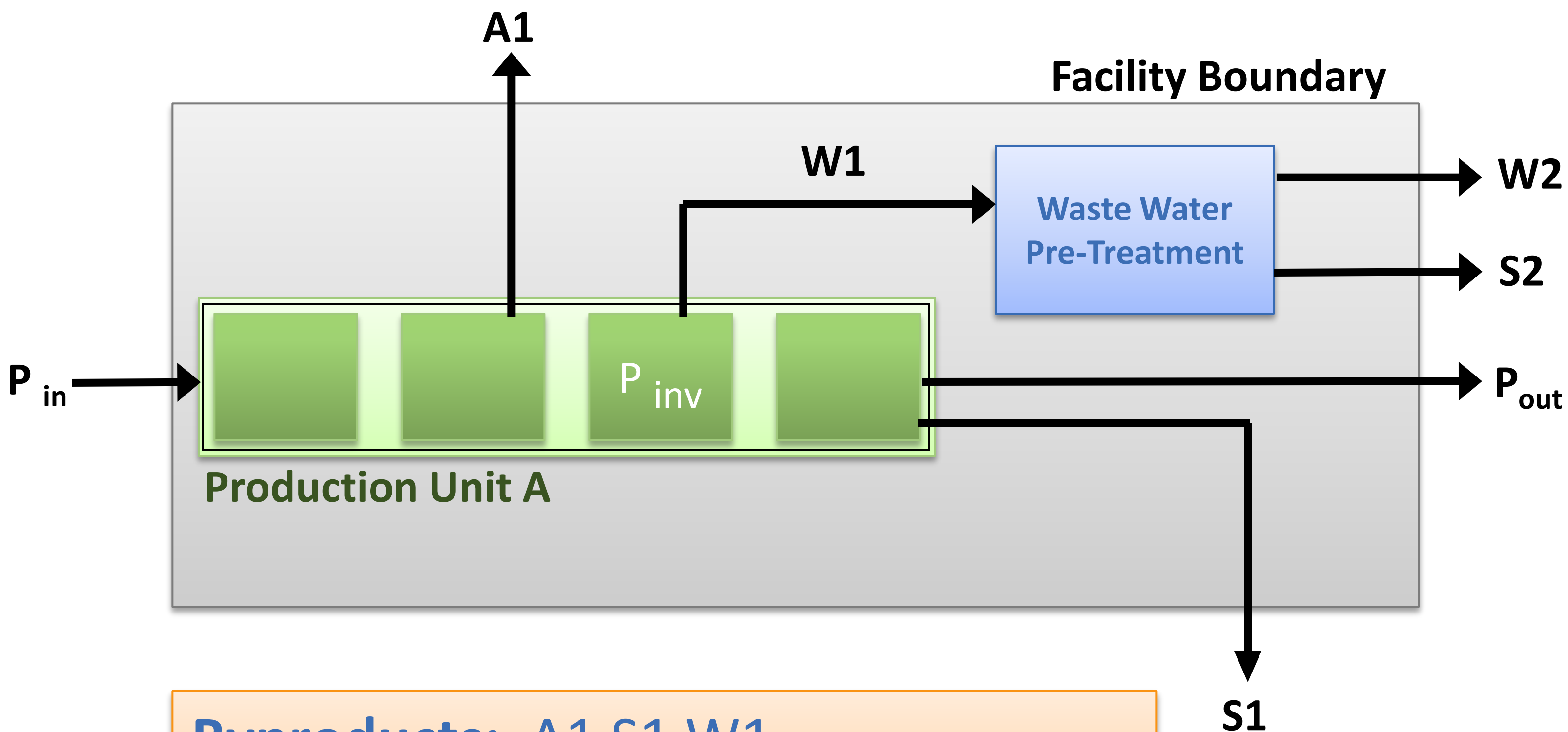
Byproduct vs. Emissions



Byproducts: A1 S1 W1

Emissions: A1 S1 S2 W2

Byproduct vs. Emissions



Byproducts: A1 S1 W1

Emissions: A1 S1 S2 W2

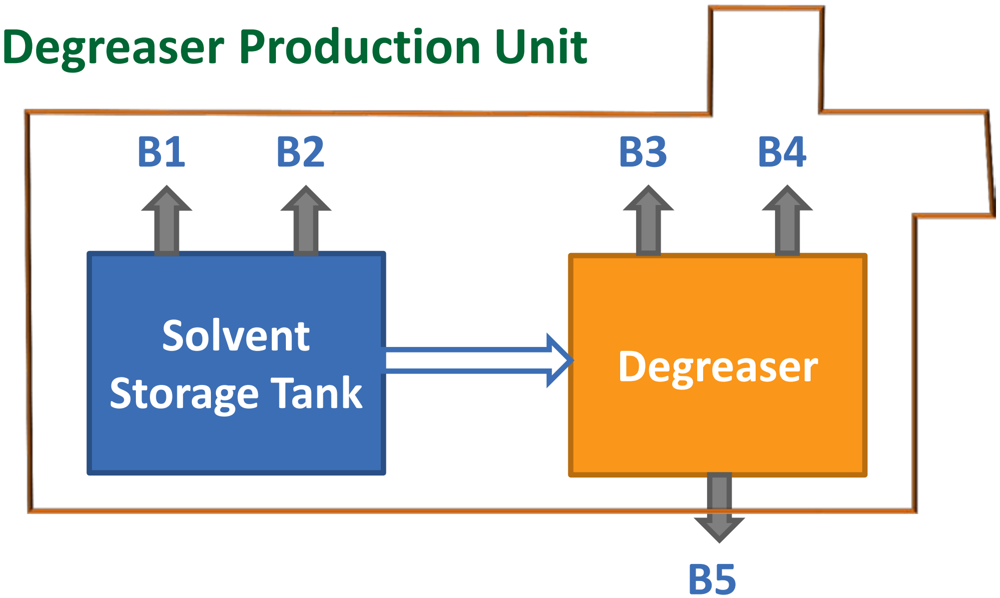
Byproduct and Emission Determination

Use Existing Data Sources

- **Direct Measurements --** continuous and non-continuous (extrapolations from periodic monitoring)
- **Engineering and Design Calculations**
- **Best Engineering Judgment Estimates**
- **Vendor specs and data**

Byproduct and Emission Generation

Example: Vapor Degreaser Production Unit

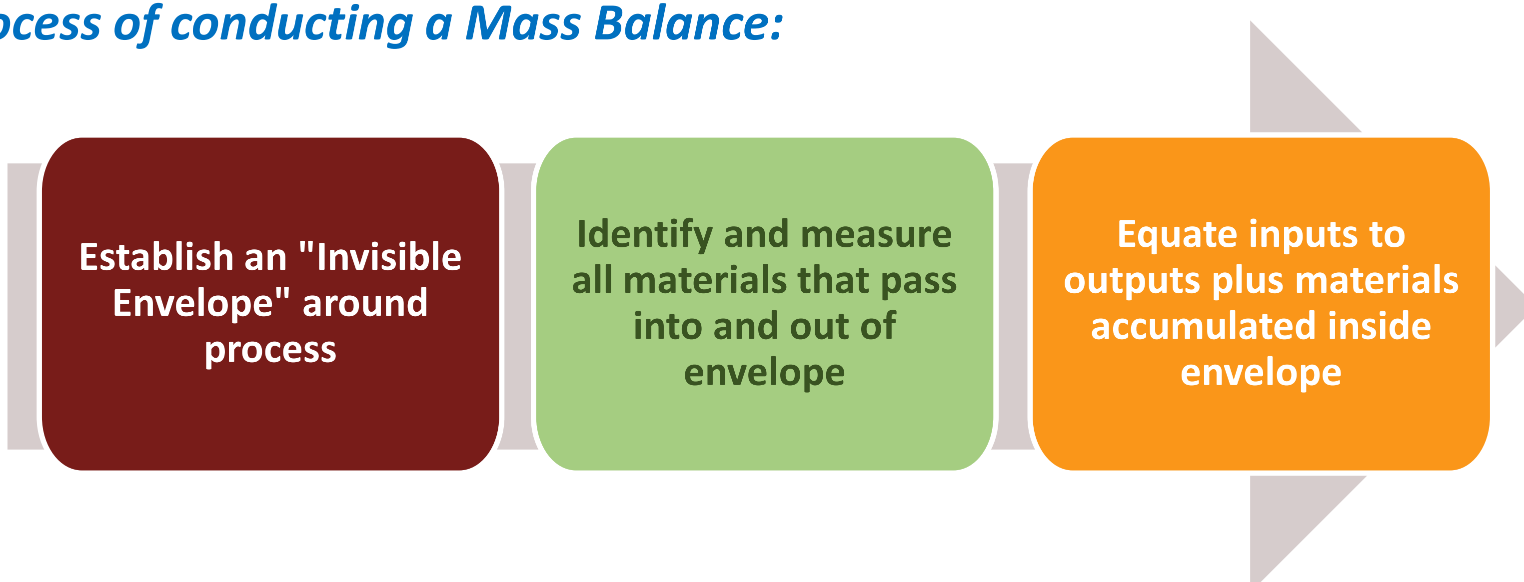


	Byproduct / Emission	Is related to
B1	Losses during solvent delivery	Number of Deliveries
B2	Volatilization from tank vent	Temperature Differences
B3	Fugitive (Operating Losses)	Hours of Operation
B4	Fugitive (Drag-out)	Number of Parts/Lots
B5	Hazardous Waste Generation	Soil Loading and Humidity

Mass Balance

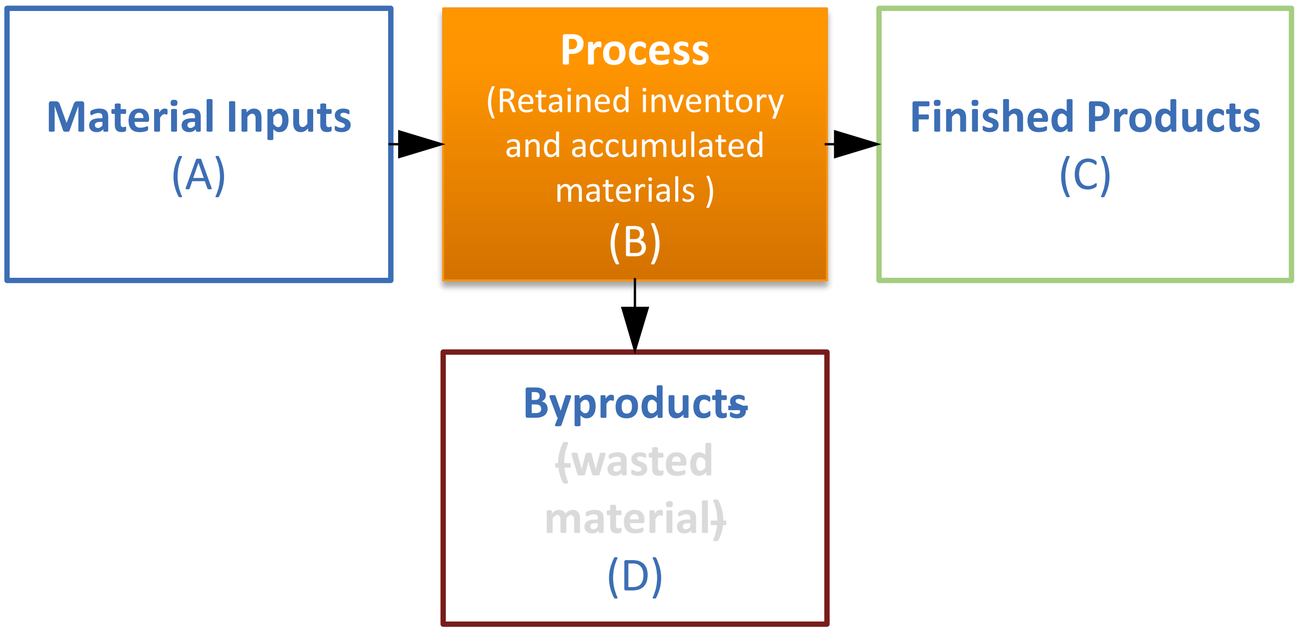
An accounting technique that equates the materials put into a process with materials released by the same process.

Process of conducting a Mass Balance:



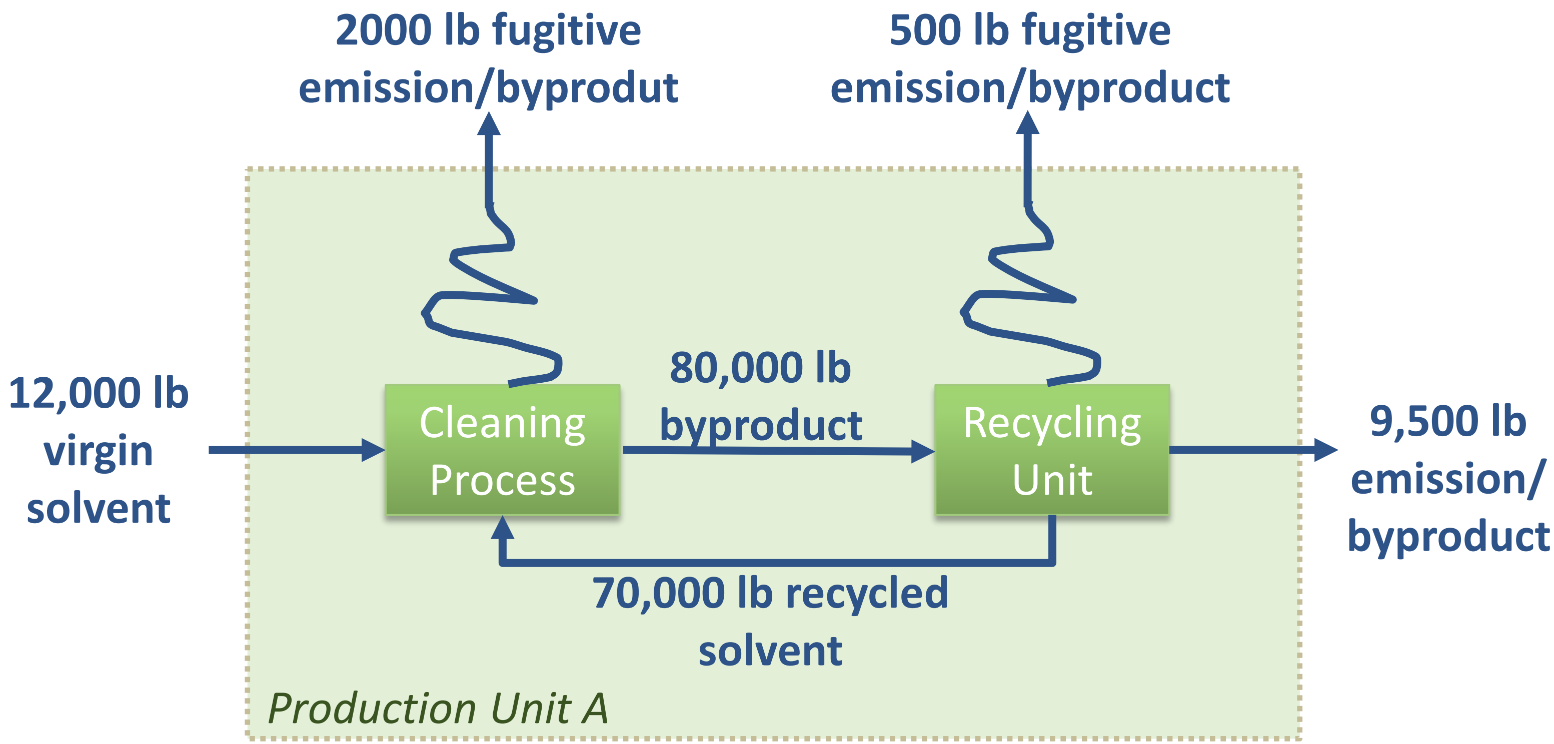
Mass Balancing

Material In = Material Out + Material maintained in Process
- Material consumed in process



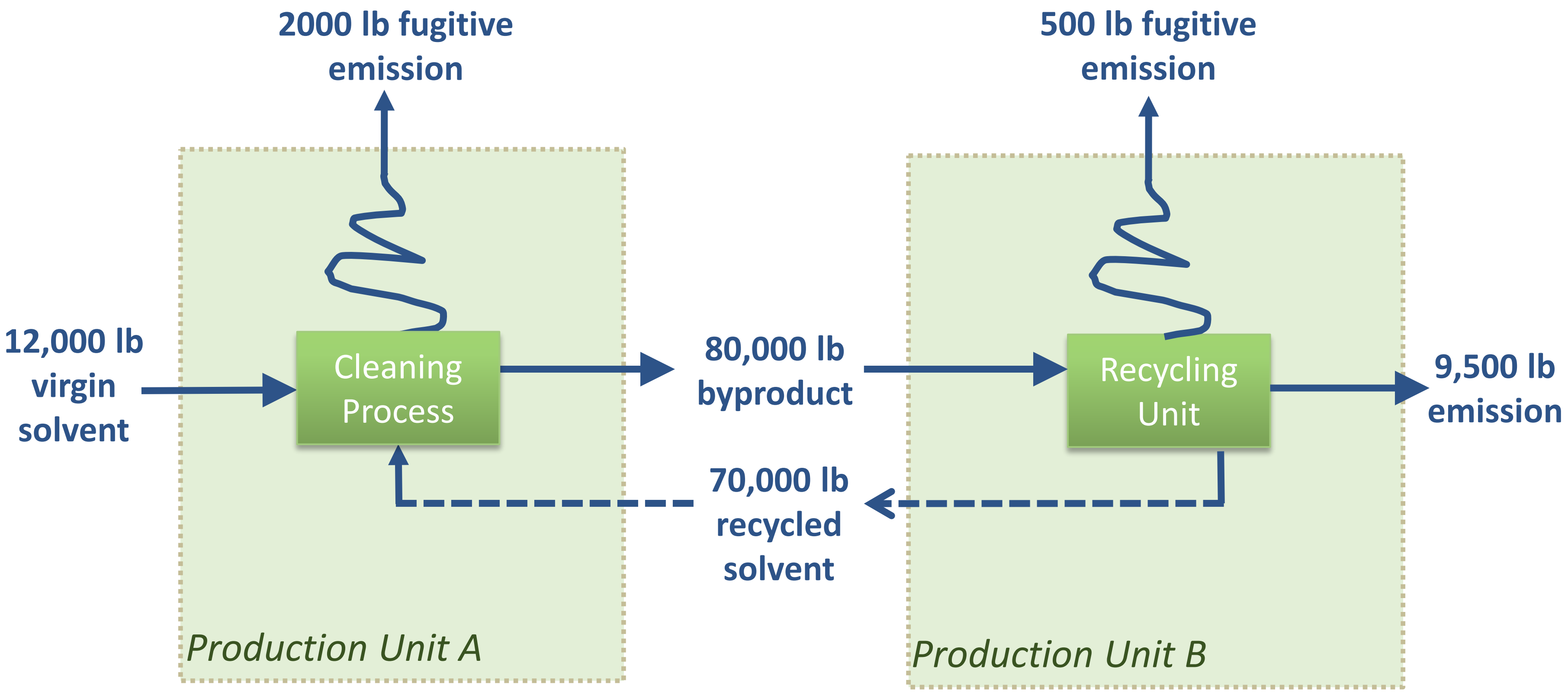
$$A = (C + D) + B$$

Mass Balance: Defining the System



Production Unit Mass Balance:
In = Out + Accumulated
12,000 lb = 9,500 lb + 2,000 lb + 500 lb + 0

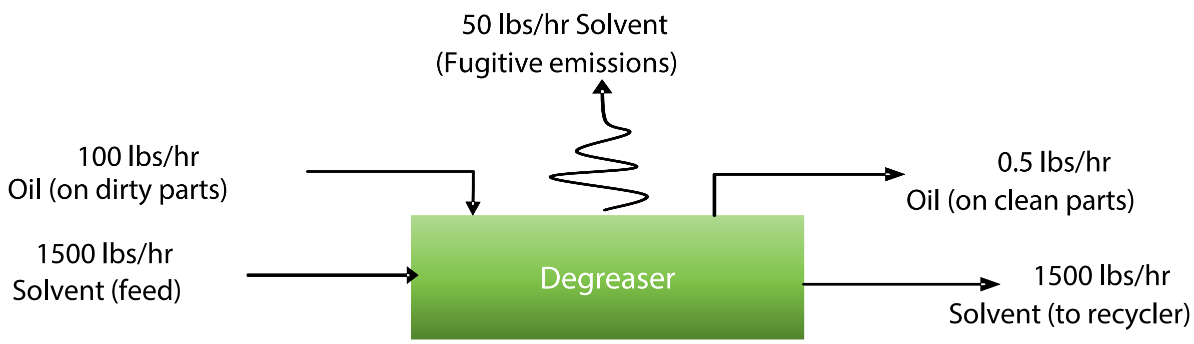
Mass Balance: Defining the System



Production Unit A Mass Balance:
In = Out + Accumulated
12,000 lb + 70,000 lb =
80,000 lb + 2,000 lb + 0

Production Unit B Mass Balance:
In = Out + Accumulated
80,000 lb =
70,000 lb + 9,500 lb + 500 lb + 0

Accounting for Accumulation



Calculate the amount of oil accumulated and solvent lost in an 8-hour day

Oil Mass Balance:

In	**=**	**Out**	**+**	**Accum**
(100 lbs/hr)(8 hrs)	=	(0.5 lb/hr)(8 hr)	+	Accum
800 lb	=	4 lb	+	Accum
Accum	=	796 lb.		

Solvent Mass Balance:

In	**=**	**Out**	**+**	**Accum**
(1500 lbs/hr)(8 hrs)	=	(1500 lb/hr)(8 hr) + (50 lb/hr)(8hr)	+	Accum
12,000 lb	=	12,000 lb + 400 lb	+	Accum
Accum	=	- 400 lb.		

Data Sources: Byproducts and Emissions

Materials as Byproducts and Emissions

- Waste Transport Manifests and Invoices
- Media-specific Environmental Reports
- POTW, NPDES, Air Pollution Source Registration, Biennial Waste Reports
- Prior TRI Reports
- Spill/Release Reports

Materials Reused or Recycled

- Recycling Records:
  - Recycler Invoices
  - Recycling Permits
  - Scrap Logs

Sources Of Chemical Use Data

Toxic Chemical Procurement (Purchasing)

- Raw Material Purchasing Records
- Vendor Invoices
- Transfer Records (between facilities)

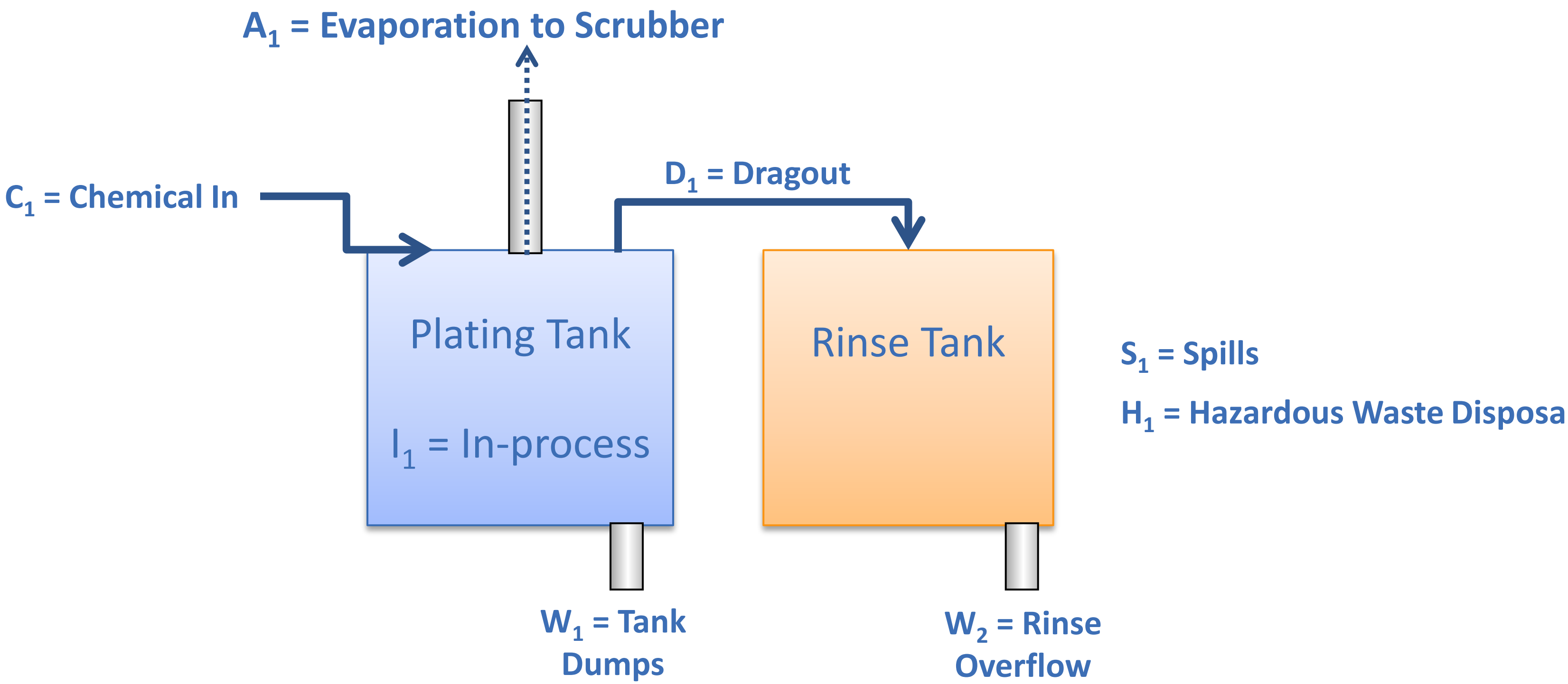
Toxic Chemical as Inventory

- End-of-Year Inventory Records
- Storage/Warehouse Records
  - Potential source of Material Losses (e.g., leaks, evaporation, theft)
- Production Run Data, Batch Tickets, etc.

Toxic Chemical Reuse/Recycling

- Hauling / pickup records and manifests
- Sales records (if byproduct being reused as product by another)

Plating Shop Example



$$C_1 = A_1 + D_1 + W_1 + H_1 + S_1$$
$$D_1 = W_2$$

Plating Shop
Pollution Prevention Options

- Prevent drag-out (reduce D_1)
- Use recovery technology*
  (return D_1 to process tank)
- Base tank dumps on tank analysis
  (reduce W_1 and H_1)
- Train operators to minimize spills (reduce S_1)
- Cover tank when not in use (reduce A_1)
- Implement preventative maintenance programs
  (reduce S_1)
  - * reverse osmosis, ion exchange or electrolytic recovery

Individual Exercises (30 min)

- We'll go through the following 5 examples of materials accounting calculations to check for understanding
  - Work through each individually and then have short group discussion
  - Finish up during lunch, if you'd like
- Solutions will be provided afterwards

Problem 1: Product impurity concentration

Scrap tires are ground up to create crumb rubber, which is used as cushioning infill in artificial turf fields, as filler in paving material, as filler in molded and extruded products, and for a variety of other uses.

Sample testing of manufactured crumb rubber indicates that there is a concentration of 56 ppm of Lead (Pb) in the product. If 2000 tons of crumb rubber are produced in a year, how much Lead is processed? Does this amount need to be reported under TRI? (The reporting threshold for Lead is 100 lbs.)

Problem 1: Product impurity concentration - Solution

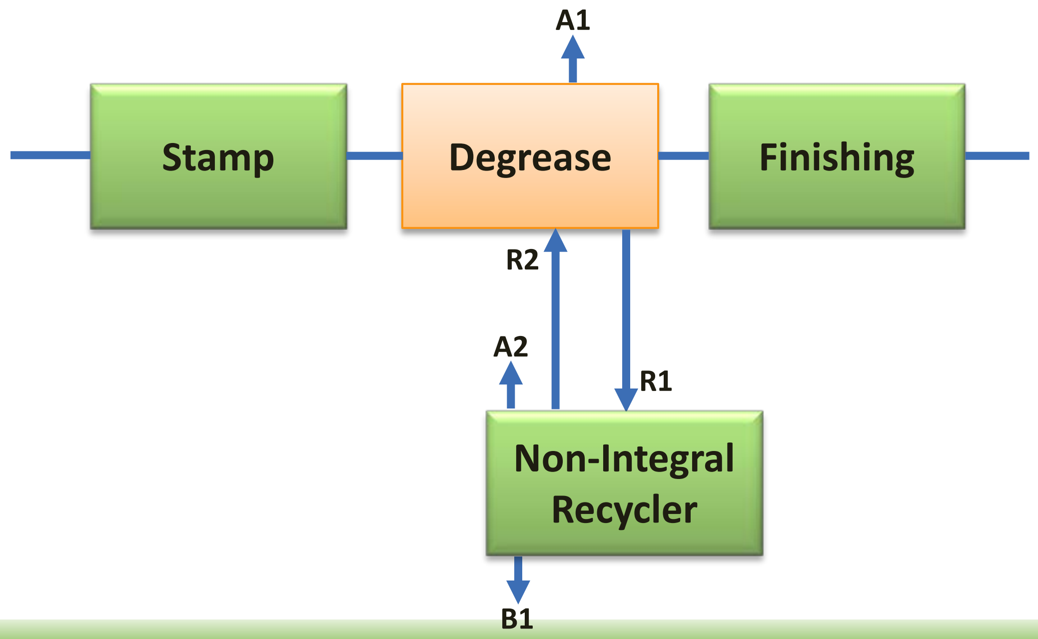
2000 tons x 2000 lbs/ton x 56×10^{-6} = 224 lbs.

Yes, since this amount of lead is greater than the threshold, it must be reported.

Problem 2: Byproduct Calculation

Calculate the Total Byproduct and Emissions

Production Unit B is a vapor degrease operation. The company purchased 4,500 lbs of TCE to operate this production unit for one year. The fugitive emissions from the degreaser (A1) were determined to be 20% of the amount of TCE used in the degreaser. The fugitive emissions from the recycler (A2) were determined to be 5.0% of the TCE sent to the recycler. The spent TCE sent from the degreaser to the recycler was 10,000 lbs for the year. The recycling process recovered 80% of the TCE that was sent to it.



- A1 – Fugitive emissions
- A2 – Fugitive emissions
- B1 – Incinerated solvent
- R1 – Spent solvent to recycler
- R2 – Recycled solvent
- P – Purchased solvent
- S – Solvent used in degreaser

Problem 2: Byproduct Calculation-Solution

<u>Given</u>

R1 = 10,000 lbs

A2 = R1 x 5.0% = 500 lbs

R2 = R1 x 80% = 8,000 lbs

P = 4,500 lbs

<u>Equations</u>

S = P + R2 = 12,500 lbs

A1 = S x 20% = 2,500 lbs

B1 = R1 – R2 – A2 = 1,500 lbs

<u>Byproduct</u>

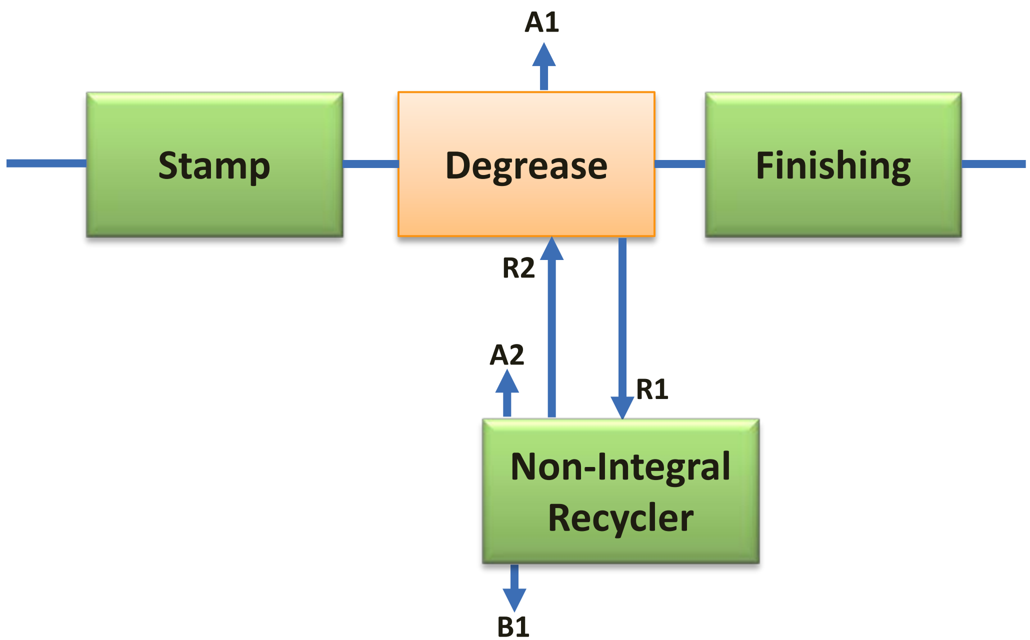
Byproduct = R1+ A1

= 12,500 lbs

<u>Emissions</u>

Emissions = A1 + A2 + B1

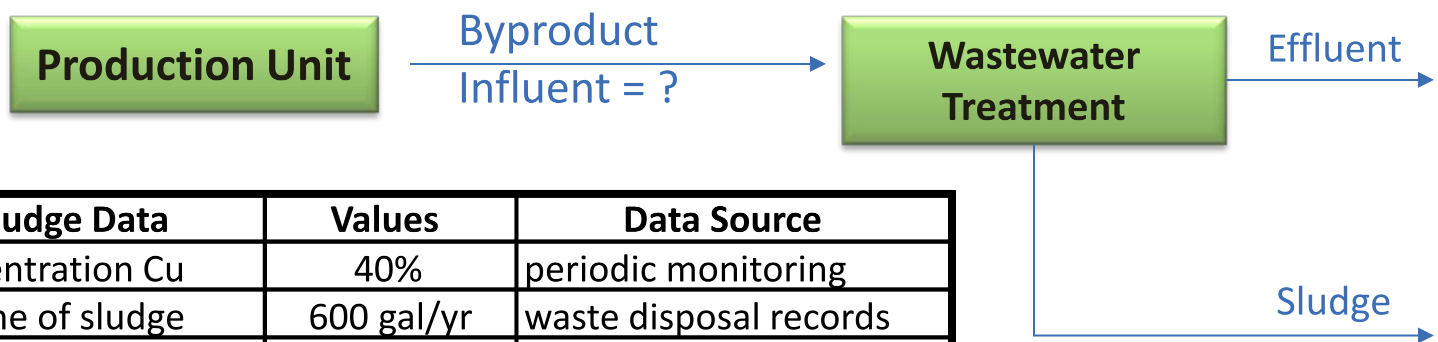
= 4,500 lbs



A1 – Fugitive emissions
A2 – Fugitive emissions
B1 – Incinerated solvent
R1 – Spent solvent to recycler
R2 – Recycled solvent
P – Purchased solvent
S – Solvent used in degreaser

Problem 3: Back-Calculating Byproduct from Treatment Records

Calculate the annual byproduct generation of copper



Sludge Data	Values	Data Source
concentration Cu	40%	periodic monitoring
volume of sludge	600 gal/yr	waste disposal records
density of sludge	30 lb/gal	lab results
Effluent Data		
Cu conc. in effluent	2.8 ppm	monitoring
avg flow of effluent	0.030 MGD	POTW, flow meter

Assumptions

- Concentration by weight
- Volume includes all constituents, not just copper
- Production time is 255 days/year

Problem 3: Back-Calculating Byproduct from Treatment Records

$$M_{Byproduct} = M_{Effluent} + M_{Sludge}$$

$$M_{sludge} = (30\ lb/gal)(600\ gal/yr)(40\%) = 7{,}200\ lb/year$$

$$M_{Effluent} = (0.030 \times 10^6\ gal/day)(255\ days/yr)(2.8\ part/10^6\ part)(8.34\ lb/gal)$$
$$= 179\ lb/year$$

$$M_{Byproduct} = M_{Effluent} + M_{sludge}$$
$$= 7{,}400\ lbs/year$$

Problem 4: Non-integral Recycling

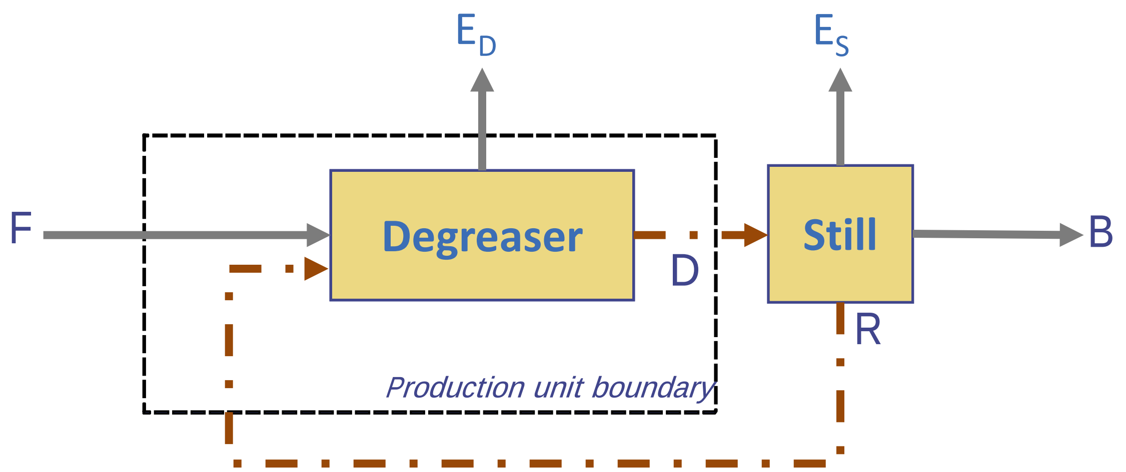
One production unit at a facility is a toluene degreasing step. Fresh toluene is added to an open-top degreaser at a rate of 8000 lb/yr. 75% of the total toluene input is lost to evaporation, the rest is sent to a non-integral recycling still. 2,000 lb/yr of recycled toluene from the still is added back to the degreaser. The still loses 15% of the total in it to evaporation. The still bottoms are sent off-site as hazardous waste. The process is at steady state.

a. Draw a process flow diagram of this production unit.

b. Calculate the total emissions and total byproducts from this production unit.

c. Consider that the production unit scenario above was for 2008. In 2011 the company hard-piped the still to the degreaser. What are the byproduct and emissions for 2011?

Problem 4: Non-Integral Recycling - Solution



GIVEN

$F = 8{,}000$ lb $\quad E_D = 0.75 * (F + R)$

$R = 2{,}000$ lb $\quad E_S = 0.15 * D$

Production Unit Balance

$F = B + E_D + E_S$

Degreaser

$D = F + R - E_D$

Still

$B = D - R - E_S$

5 equations, 4 unknowns:

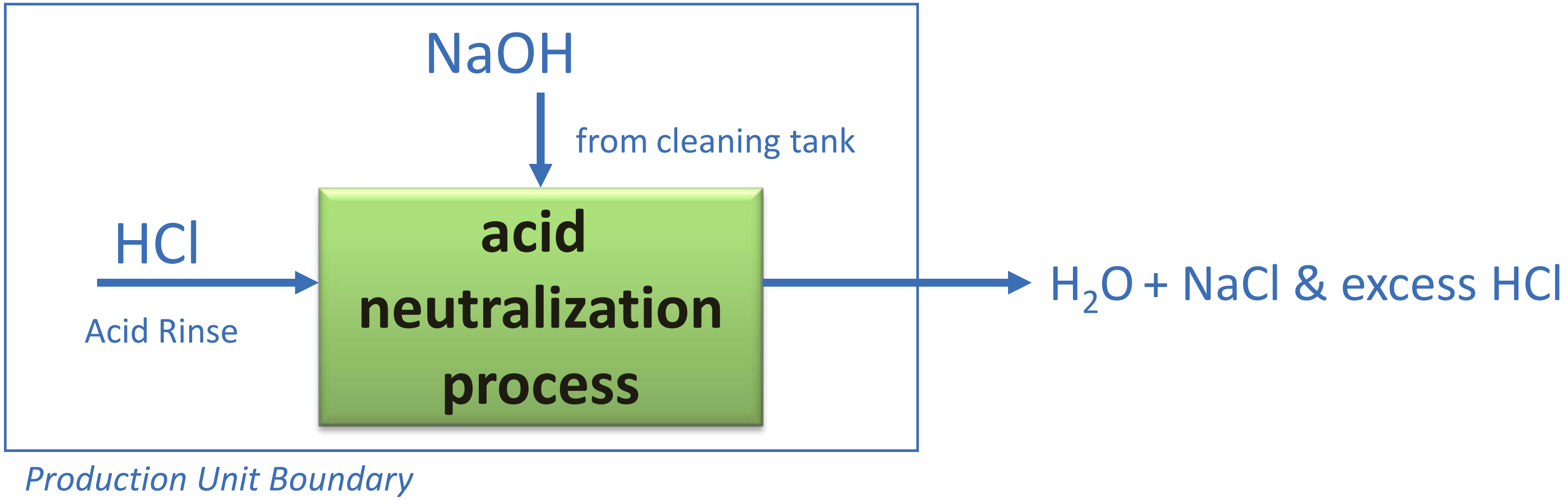
$E_D = (0.75)(10{,}000 \text{ lb}) = 7{,}500 \text{ lb}$

$D = 10{,}000 - 7{,}500 \text{ lb} = 2{,}500 \text{ lb}$

$E_S = (0.15)(2{,}500 \text{ lb}) = 375 \text{ lb}$

$B = 2{,}500 \text{ lb} - 2{,}000 \text{ lb} - 375 \text{ lb} = 125 \text{ lb}$

Problem 5:
Byproduct from a Known Reaction



Determine the resulting byproduct if 1500 lb of NaOH is added to: 15,000 pounds of HCl

	Quantity added	M.W.
	(lb)	(lb/lb-mol)
Base (NaOH)	1500	40.0
Acid (HCl)	15,000	36.5

Problem 5: Byproduct from a Known Reaction - Reportable Amounts

HCl reacts with NaOH to produce H_2O & NaCl

If the amount of NaOH is ***not*** sufficient to neutralize the amount of HCl, un-neutralized HCl will remain

The reaction amounts can be calculated from known inputs of NaOH and HCl

Reportable HCl use: 15,000 lbs (given)

Reportable NaOH use: 1,500 lbs (given)

HCl neutralized: 1370 lbs (from chemical equation – see next slide)

Reportable HCl byproduct = (15,000 lb HCl in) – (1,370 lb HCl neutralized) = 13,600 lb HCl

NaCl is not a listed chemical

Problem 5: Byproduct from a Known Reaction - Solution

Reaction equation:

$HCl + NaOH \Rightarrow H_2O + NaCl$

i.e., one mole HCl reacts with one mole NaCl to create 1 mole H_2O and 1 mole NaCl

$$1500\ \cancel{lb\ NaOH} \times \frac{\cancel{lb-mol\ NaOH}}{40\ \cancel{lb\ NaOH}} \times \frac{36.5\ lb\ HCl}{\cancel{lb-mol\ HCl}} \times \frac{1\ \cancel{lb-mol\ HCl}}{1\ \cancel{lb-mol\ NaOH}}$$

$= 1370\ lb\ HCl$ neutralized

(calculated to 3 significant figures)

Reportable byproduct = (15,000 lb HCl in) – (1,370 lb HCl neutralized) = 13,600 lb HCL

One accurate measurement is worth a thousand expert opinions.

Admiral Grace Hopper
US Navy